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Assembling of $H_5PW_{10}V_2O_{40}$/MCM-48 and studying its superior catalytic performance in the synthesis of 14-aryl-14-H-dibenzo[a, j]xanthenes

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Abstract. A highly efficient, green, and reusable heterogeneous catalytic system is introduced for the preparation of aryl-14-H-dibenzo[a,j]xanthenes via one-pot condensation of β-naphthol with aryl-aldehydes by the mediation of a heterogeneous material composed of *Keggin*-type tungsto-divanado-phosphoric acid, $H_5PW_{10}V_2O_{40}$, supported on MCM-48 under solvent-free condition. Excellent yields (85–100%), short reaction time (<60 min.), mild condition, simple work-up, and using a cheap and environmentally friendly catalyst bearing remarkable reusability are advantages of the present methodology. The catalytic efficacy of $H_5PW_{10}V_2O_{40}$/MCM-48 over some reported protocols are also overviewed.

Keywords. Xanthene; heteropolyacid; keggin; solvent-free; heterogeneous; MCM-48.

1. Introduction

The increasing applications of catalyst-based synthetic methods in emerging industries have been favoured by the continuous innovations observed over the last decade for different catalytic processes.[1] Catalysis based on heteropolyacids (HPAs) and related compounds, especially those comprising the strongest *Keggin*-type HPAs, is an important field in which new and promising developments are being carried out in both academia and technological fields.[2] The major disadvantages of heteropolyacids lie in extremely low surface area, water-solubility, hard recovery and recycling which always limit their practical applications.[3,4] Utilization of heterogeneous catalysts in organic synthesis seems to be one of the most attractive ways to avoid the above mentioned problems and referred to as environmentally benign catalysts for their nonpolluting properties. In general, heterogeneous catalysts offer higher surface area, lower coordinating sites, high atom efficiency, easy product purification, and simple reusability.

MCM-48 is a class of mesoporous silica tube-like materials with uniformly sized three-dimensional mesopores. These compounds have been of interest as sorbent and solid support in catalysis.[5,6] The mesoporous silica material MCM-48 has been considered as an ideal support for various HPAs, because of its large surface area and special pore structure, moreover, this support is easier to be produced at a low cost.

Xanthenes and benzoxanthene derivatives are biologically important drug intermediates in the field of medicinal chemistry for their biologically active properties, such as antimalarial,[7] antibacterial,[8] antiinflammatory,[9] and antiviral properties.[8] Among them, xanthenediones form the structural unit in many of the natural product compounds[10,11] and are used as versatile synthons for their inherent reactivity[12] due to the presence of inbuilt pyran ring. Xanthenediones have been synthesized by various procedures via condensation of appropriate active methylene carbonyl compounds with aldehydes.[13] These compounds are usually formed from condensation of active methylene carbonyl compounds with aldehydes in the presence of various Lewis acids. Furthermore, 14-H-dibenzo[a,j]xanthenes and their analogues are synthesized from the reaction of 2-naphthol with 2-naphthol-1-methanol,[14] formamide,[15] carbon monoxide,[16] aldehydes[17] and aldehyde acetals.[18] Although, most of the reported homogeneous and heterogeneous catalytic systems have exhibited acceptable efficacy, however, many of them suffer from certain drawbacks including corrosive and harmful nature, long reaction time, unsatisfactory yield, harsh reaction condition, difficulty in reusability, and excessive use of reagents and catalysts.

In order to overcome these common drawbacks, considerable efforts have been achieved to the development

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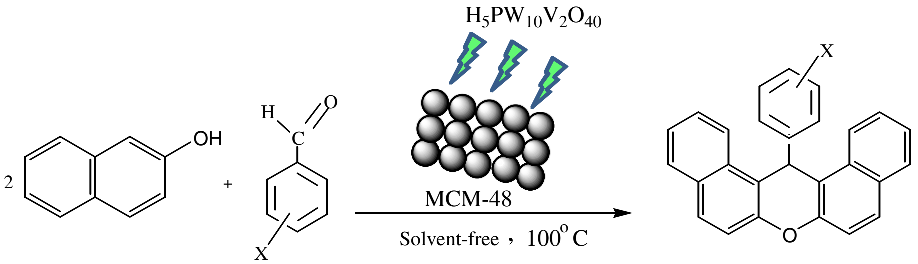


Scheme 1. General formulation for the synthesis of aryl-14-H-dibenzo[a,j]xanthenes.

of heterogeneously catalysed organic reactions using solid acid catalysts such as zeolites,[19] clays,[20] and ion exchange resins.[21]

In continuation of our previous works to develop non-hazardous and eco-friendly synthetic methodologies,[22–25] here we wish to report a highly versatile, eco-friendly, and efficient one pot heterogeneous protocol for the synthesis of aryl-14-H-dibenzo[a,j]xanthene derivatives from condensation of aldehydes and 2-naphthol catalysed by a catalytic amount of heterogenized $H_5PW_{10}V_2O_{40}$/MCM-48 under solvent-free condition (scheme 1). The experimental procedure for this reaction is remarkably simple and requires no toxic organic solvents or inert atmosphere.

$H_5PW_{10}V_2O_{40}$/MCM-48 was prepared by loading of $H_5PW_{10}V_2O_{40}$ on siliceous MCM-48 via the wet impregnation method and was characterized by means of spectroscopic instruments. The reactions were carried out at 100°C for <1 h by taking a 1:2 mol ratio mixture of aldehyde: β-naphthol in the presence of 0.06 g catalyst.

2. Experimental

Reagents and starting materials were purchased from commercial resources and were used as received. All products were identified by comparison of their spectral and physical data with those previously reported.[26,27] Progress of the reactions was monitored by TLC. Infrared spectra were recorded (KBr pellets) on a 8700 *Shimadzu* Fourier Transform spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 100-MHz instrument using TMS as an internal reference. Data for ^1H NMR are reported as follows: chemical shift (δ) and multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, qt: quintuple, dq: doublet of quartets, br: broad).

2.1 *Preparation of 10-Tungsto-2-vanadophosphoric acid $H_5PW_{10}V_2O_{40}.30H_2O$*[28]

Sodium metavanadate ($NaVO_3$, 12.2 g, 100 mmol) was dissolved in 50 ml of boiling water and mixed with di-sodium hydrogen phosphate (Na_2HPO_4, 3.55 g, 25 mmol), dissolved in 50 ml of water. After the resulting solution was cooled to room temperature, concentrated sulphuric acid (5 mL, 17 M, 85 mmol) was added to give a red solution. Sodium tungstate dihydrate (Na_2WO_4. $2H_2O$, 82.5 g, 250 mmol) was dissolved in 100 ml of water and was added to a red solution with vigorous stirring, followed by the slow addition of concentrated sulphuric acid (42 ml, 17 M, 714 mmol). Extraction of the solution with diethyl ether (500 mL), followed by evaporation in air, afforded $H_5PW_{10}V_2O_{40}$ as a crystalline, orange-red solid (yield, 74%). Calcd (Found): P, 0.98 (1.05); W, 58.24 (58.12); V, 3.22 (3.16); H_2O, 17.12 (17.26). FT-IR (KBr): 1070(s), 980(vs), 885(s), 788(vs) cm^{-1}.

2.2 *Synthesis of MCM-48, conventional hydrothermal synthesis*[29]

n-Hexadecyltrimethylammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$, template) was dissolved in deionized water, and sodium hydroxide and tetraethoxysilane (TEOS) were added. The molar composition of the gel was 1 M TEOS/0.25M Na_2O/0.65 M $C_{16}H_{33}(CH_3)_3NBr$/62M H_2O. The solution was stirred for about 1 h, charged into a polypropylene bottle and then heated at 383 K for 3 days. The product was filtered, washed with water and calcined at 823 K for 6 h.

2.3 *Preparation of supported catalysts*[26]

The MCM-48 supported $H_5PW_{10}V_2O_{40}.30\ H_2O$ was prepared by mixing the dried MCM-48 (1 g) with a solution of $H_5PW_{10}V_2O_{40}.30\ H_2O$ (0.25 g) in the minimum amount of deionized water. The resulting mixture was stirred continuously with a magnetic stirrer for 12 h. After removal of water, the solid powder was first dried at 100°C for 4–5 h, then dried at 140°C for 2 h.

2.4 *General procedure for the synthesis of aryl-14-H-dibenzo[a,j]xanthenes*

A mixture of 2-naphthol (2 mmol), aldehyde (1 mmol) and 0.06 g MCM 48-$H_5PW_{10}V_2O_{40}$ was heated at 110°C for an appropriate time (monitored by TLC, 2:1 petroleum ether:ethyl acetate). After cooling, the reaction mixture was washed with $CHCl_3$ (10 mL) to remove the un-reacted aldehyde. The solvent was evaporated and the crude product was re-crystallized from EtOH to afford the pure product.

2.5 *Spectral data for selected 14-aryl-14-H-dibenzo[a, j] xanthenes*

2.5a *14-(4-Chlorophenyl)-14H-dibenzo[a,j]xanthenes*: Brown solid; ^{1}H NMR ($CDCl_3$, δ_{ppm}): 8.29 (d, *J* 8.46 Hz, 2H), 7.83–7.77 (m, 4H), 7.58–7.54 (m, 2H), 7.47 (s, 1H), 7.45–7.38 (m, 5H), 7.10–7.07 (m, 2H), 6.44 (s, 1H); ^{13}C NMR: 156.0, 147.8, 132.8, 131.2, 129.3, 128.8, 128.3, 127.0, 126.8, 126.5, 124.7, 119.3, 118.2, 117.8, 33.5; IR (KBr, cm^{-1}): 3050, 2925, 1620, 1595, 1456, 1431, 1396, 1242, 1060, 960, 824, 778, 695; EI-MS: $m/z(\%) = 392$ (M^+); Anal. Calcd for $C_{27}H_{17}ClO$: C, 82.54; H, 4.36. Found: C, 82.46; H, 4.44.

2.5b *14-(4-Nitrophenyl)-14H-dibenzo[a,j]xanthenes*: Yellow solid; ^{1}H NMR ($CDCl_3$, δ_{ppm}): 8.29 (2H, d, *J* 8.4 Hz),7.99 (2H, d, *J* 8.7 Hz), 7.86 (2H, d, *J* 4.1 Hz), 7.82 (2H,d, *J* 5.4 Hz), 7.67 (2H, d, *J* 8.8 Hz), 7.61 (2H, t, *J* 5.6 Hz),7.51 (2H, d, *J* 8.9 Hz), 7.44 (2H, t, *J* 7.9 Hz), 6.60 (1H, s); IR (KBr, cm^{-1}): 3070, 2930, 1621, 1591, 1614, 1457, 1400, 1340, 1200, 1140, 1105, 1013, 964, 851, 827, 808, 742, 690. EI-MS:$m/z(\%) = 403$ (M^+); Anal. Calcd for $C_{27}H_{17}NO_3$: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.30; H, 4.35; N, 3.55.

2.5c *14-(3-Chlorophenyl)-14H-dibenzo[a. j]xanthenes*: Brown solid; ^{1}H NMR ($CDCl_3$, δ_{ppm}): 8.30 (d, *J* 8.4 Hz, 2H), 7.86 (d, *J* 8.6 Hz, 2H), 7.76 (d, *J* 9.0 Hz, 2H), 7.60 (t, *J* 7.0 Hz, 2H), 7.50 (d, *J* 8.9 Hz, 2H), 7.48–7.43 (m, 4H), 7.10 (t, *J* 8.0 Hz, 1H), 6.96 (d, *J* 8.7 Hz, 1H), 6.45 (1H, s); ^{13}C NMR: 148.5, 146.8, 134.5, 131.2, 131.0, 129.7, 129.1, 128.8, 128.2, 127.1, 126.8, 126.4, 124.5, 122.4, 118.1, 116.4, 37.8; IR (KBr, cm^{-1}): 3053, 2926, 1622, 1590, 1508, 1455, 1430, 1398, 1245, 1064, 959, 815, 775, 745, 690; EI-MS:$m/z(\%) = 392$ (M^+); Anal. Calcd for $C_{27}H_{17}ClO$: C, 82.54; H, 4.36. Found: C, 82.48; H, 4.42.

2.5d *14-(4-Bromophenyl)-14-H-dibenzo[a,j]xanthenes*: ^{1}H NMR ($CDCl_3$, δ_{ppm}): 8.30 (s, 1H), 8.28 (s, 1H), 7.83 (s, 1H), 7.81 (s, 1H), 7.79 (s, 1H), 7.77 (s, 1H), 7.56 (t, *J* 6.96 Hz, 2H), 7.47 (s, 1H), 7.45 (s, 1H), 7.42 (s, 1H), 7.40 (s, 1H), 7.38 (s, 1H), 7.36 (s, 1H), 7.24 (d, *J* 2.93 Hz, 2H), 6.43 (s, 1H); ^{13}C NMR: 148.66, 143.95, 131.55, 131.22, 131.03, 129.83, 129.07, 128.88, 126.88, 124.34, 122.36, 120.18, 117.97, 116.63, 37.41. IR (KBr, cm^{-1}): 3030, 1624, 1586.

3. Results and discussion

3.1 *Spectroscopic studies*

The powdered small-angle X-ray scattering of calcined mesoporous structure of MCM-48 was studied. This compound showed an intense peak assigned to the reflections at (100) and two-low intense peaks at (110) and (200), which belong to a significant degree of long-range ordering in the structure and well-ordered hexagonal pore system. The 100 reflection of the MCM-48 was still observed after the $H_5PW_{10}V_2O_{40}$ loading (figure 1). This observation confirmed that the mesoporous structure of the MCM-48 remained almost unchanged upon the heteropolyacid loading. According to Scanning Electron Microscopy (SEM) images, morphology of MCM-48 support has retained after immobilization of $H_5PW_{10}V_2O_{40}$ (figure 2).

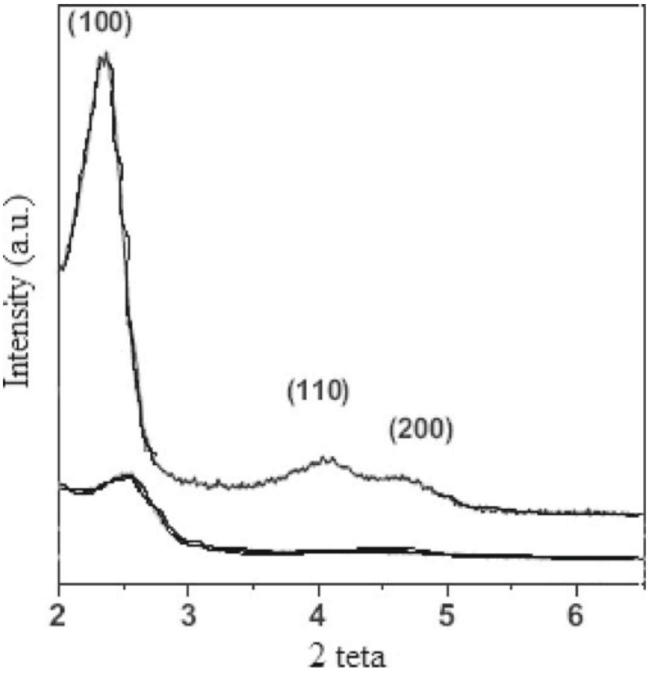


Figure 1. Low angle XRD patterns of calcined MCM-48 (up) and $H_5PW_{10}V_2O_{40}$/MCM-48 (bottom).

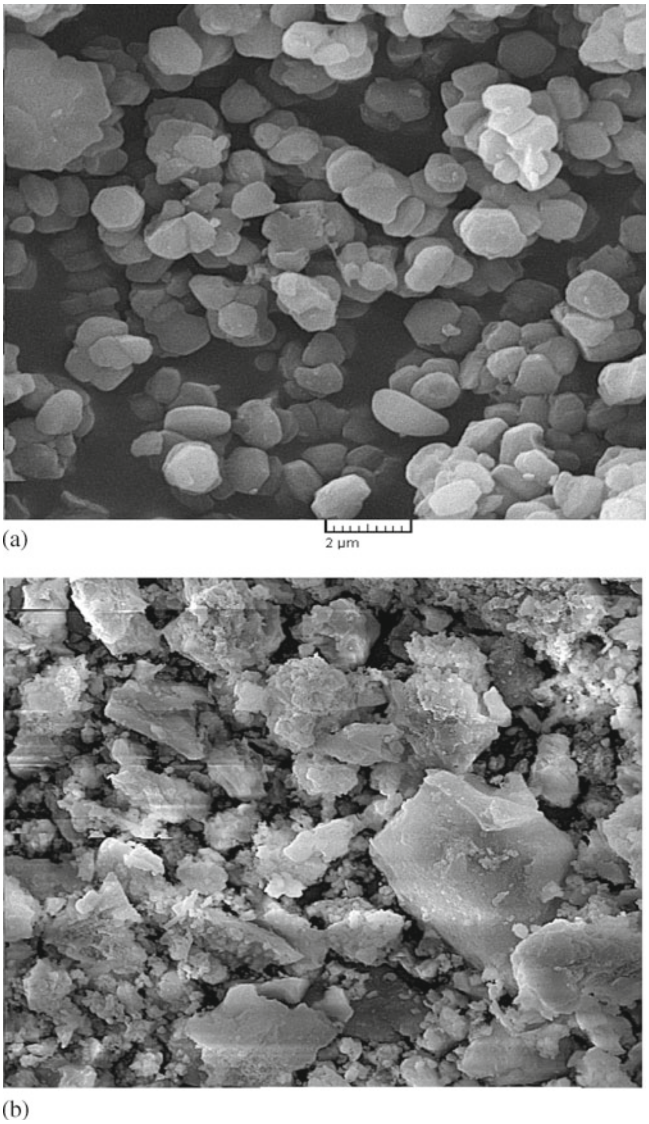


Figure 2. (**a**) SEM micrographs of MCM-48 and (**b**) $H_5PW_{10}V_2O_{40}$/MCM-48.

3.2 *Effect of the kind and concentration of vanadium substituted heteropolyacid*

The catalytic activity of $H_5PW_{10}V_2O_{40}$ was compared with other vanadium substituted heteropolyacid catalysts in the preparation of 14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene (table 1). According to our previous findings,[25] substitution of one and two vanadium atoms instead of Mo^{6+} and W^{6+} in $H_3PM_{12}O_{40}$, leading to an increase in the catalytic activity of the heteropolyacid. Meanwhile, $H_5PW_{10}V_2O_{40}$ has been a little more reactive than $H_5PMo_{10}V_2O_{40}$. Speculate catalytic activity of $H_5PW_{10}V_2O_{40}$ would be due to special coordination geometry of the complex metal oxo species and far distance of the vanadyl oxygen double bond from the heteropolyanion. This geometry exposed the vanadyl species at the surface of the heteropolyanion, which might be involved in the catalytic cycle. This realm has to be taken into account for the evaluation of the catalytic activity of $H_5PW_{10}V_2O_{40}$ and role of vanadium in the catalytic system.[30,31]

Table 1. Effect of the kind of vanadium substituted heteropolyacid catalyst in the synthesis of 14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthenes under homogeneous condition.

Heteropolyacid	Mol.%	Time (min.)	Yield (%)
$H_5PW_{10}V_2O_{40}$	0.5	80	95
$H_7SiW_9V_3O_{40}$	0.5	90	86
$H_5PMo_{10}V_2O_{40}$	0.5	90	92
$H_5SiW_9Mo_2VO_{40}$	0.5	180	96
HPA/MCM-48	0.06 g	60	99

Expectedly, the catalytic efficiency should be affected by the catalyst amount. Thus, a set of experiments using different amounts of HPA/MCM-48 was taken into account in the reaction of 4-bromobenzaldehyde and β-naphthol under solvent-free condition at 100°C (table 2). The synthetic route is drastically dependent to the presence of the catalyst and no conversion was attained in the absence of catalyst. The optimum catalyst amont was 0.06 g to reach complete conversion after 1 h. Lower amounts of catalyst resulted in a pronounced decrease in the efficacy of the protocol, while higher amounts led to complete conversion in short time, 0.5 h.

3.3 *Condensation of different aromatic aldehydes with β-naphthol*

The generality of this process was studied by a range of substituted aryl aldehydes to synthesize the corresponding dibenzo[a,j]xanthenes in high to excellent yields

Table 2. Effect of HPA/MCM-48 amount on the condensation of 4-bromo-benzaldehyde with β-naphthol.

Entry	Catalyst (g)	Time (h)	Yield (%)	Selec.%
1	—	10	<5	—
2	0.01	6	65	90
3	0.03	3	96	100
4	0.06	1	99	100
5	0.1	0.5	99	95

Reactions were carried out at 100°C by using β-naphthol (2 mmol), 4-bromo-benzaldehyde (1 mmol) and different amounts of the heteropolyacid under solvent-free condition. Progress of the reactions was monitored as described in the experimental section by TLC. Yields refer to isolated yields

Table 3. Synthesis of different xanthene derivatives catalysed by MCM-48/$H_5PW_{10}V_2O_{40}$.

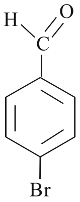
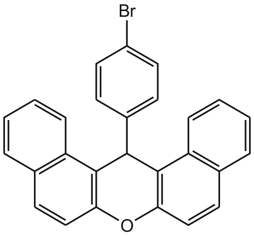
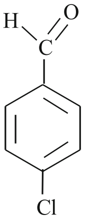
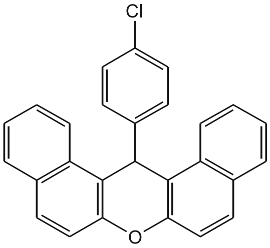
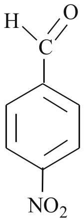
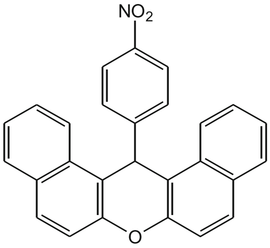
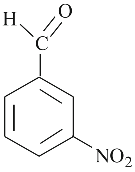
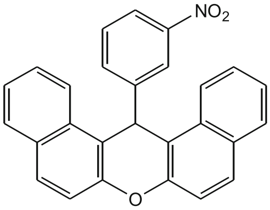
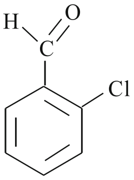
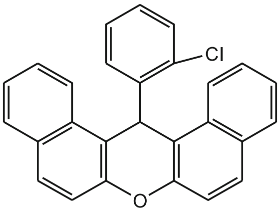
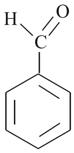
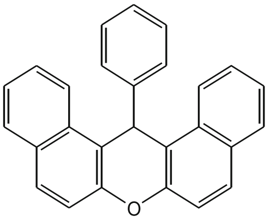
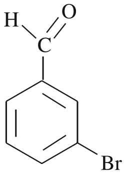
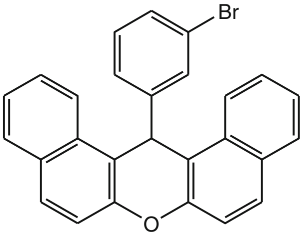
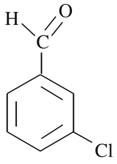
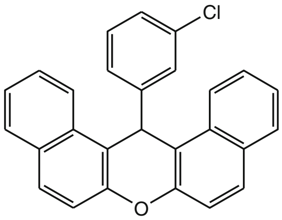
Entry	Aldehyde	Product	Time (h)	Yield (%)	Mp (°C) observed	Mp (°C) reported	Ref.
1			1	99	295–297	296	32
2			0.6	95	289–290	289–290	32
3			1	70	309–310	310	33
4			1	90	212–213	211–212	32
5			0.8	85	213–214	215	34
6			1	90	182–183	181–183	32
7			1	85	190–191	190–192	34

Table 3. *(continued)*

Entry	Aldehyde	Product	Time (h)	Yield (%)	Mp (°C) observed	Mp (°C) reported	Ref.
8			1	87	189–190	210–211	35

Reactions were carried out at 100°C by using β-naphthol (2 mmol), aromatic aldehyde (1 mmol) and 0.06 g MCM-48/$H_5PW_{10}V_2O_{40}$ under solvent-free condition. Progress of the reactions was monitored as described in the experimental section by TLC

(table 3). High yields were attained without any significant amounts of undesirable side products. The present protocol does not require toxic organic solvent to produce aryl-14-H-dibenzo[a,j]xanthenes. All products were characterized by FT-IR and comparison of melting points with literature. This general method tolerated both electron-withdrawing and electron-donating constituents and afforded the respective xanthene derivatives in high yields. It was confirmed that aldehydes were stable toward oxidation under the reported strong acidic condition.

3.4 *The excellence of MCM-48 over some well-known carriers for $H_5PW_{10}V_2O_{40}$*

The M41S family consists of three basic silicate structures, including hexagonal, cubic, and lamellar which has been designated as MCM-41, MCM-48, and MCM-50.[36] MCM-41 consists of one-dimentional parallel channels, whereas mesoporous MCM-48 contains a three-dimentional channel system with high hydrophobicity and acidity, large surface area, and high thermal and hydrothermal stability (figure 3).[37] Although table 4 reveals that textural and physicochemical properties of mesoporous MCM-41 and MCM-48 are comparable, tunable mesoporous pore size distribution of the latter, enabled this material as a potent support.[38] These structural features might be involved in the less catalytic activity of MCM-41/$H_5PW_{10}V_2O_{40}$ versus MCM-48/$H_5PW_{10}V_2O_{40}$.

To further investigate the efficacy of MCM-48 as support, some other well-known carriers such as SBA-15, MCM-41, SiO_2, and ZrO_2 were evaluated to immobilize $H_5PW_{10}V_2O_{40}$. All the catalysts were compared under similar conditions in the reaction of β-naphthol with 4-chlorobenzaldehyde (table 5). The comparison was based on the product yield, recovery, and reusability of the catalyst. MCM-48 was the best among the examined supports and led to 95% yield after 1.3 h.

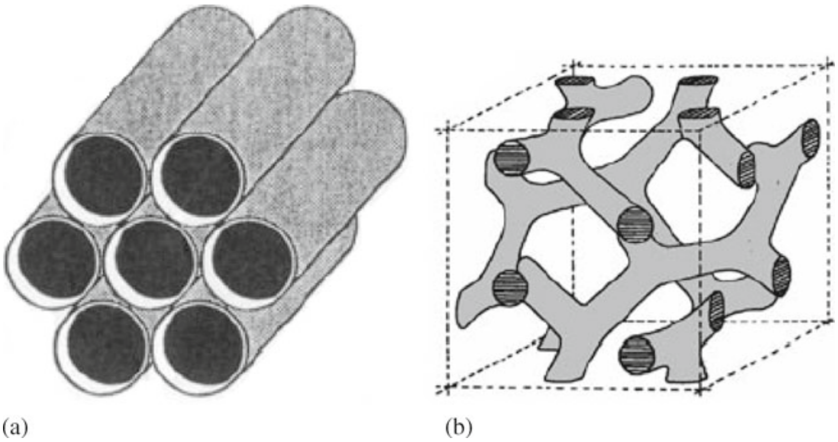


Figure 3. (**a**) Hexagonal channel arrangement of MCM-41 and (**b**) cubic array of MCM-48 channels. Data are reproduced with permission from Kresge, Bejblova *et al.*[36–38]

Table 4. Textural and physicochemical properties for mesoporous MCM-41 and MCM-48.

Support	S_{BET} (M^2/g)	Pore volume (cm^3/g)	Pore diameter (A°)
MCM-41	1155	0.88	30.5
MCM-48	1096	0.71	26.1

Data are reproduced with permission from Kresge, Bejblova *et al.*[36–38]

SBA-15 also produced the same conversion, but during longer time 1.5 h. Although, MCM-41 has comparable structure as MCM-48, the former was less effective and produced 75% of conversion after 2.5 h. 0.25 mol% $H_5PW_{10}V_2O_{40}$ embeded on 0.03 g of MCM-48 and SBA-15 produced 95–97% of conversion after 1.3–1.5 h.

ZrO_2 and SiO_2 were inefficient compared to other supporting materials, produced 60 and 37% of conversions after 3 and 4 h, respectively. Although, all the examined supports involve pores large enough to scavenge the heteropolyacid, however, different observed reactivity pattern would be attributed to the influence of internal backbone of the solid material on the reactivity of the heteropolyacid. Interestingly, in comparison with the unsupported homogeneous system, the catalytic activity of $H_5PW_{10}V_2O_{40}$ was increased by immobilization onto MCM-48. Thus, it seems that the solid support would activate the catalyst molecules into the desired synthesis route. However, for other supports, the catalytic activity of HPA was declined as a result of immobilization. These observations would be explained considering changes occurred in the acid strength of the HPA due to its interaction with the solid support. Using 0.015 g $H_5PW_{10}V_2O_{40}$ supported on 0.06 g MCM-48 led to the formation of 95% product after 0.6 h, whereas the same amount of catalyst led to the same conversion after 1.3 h in the homogeneous condition. These findings clearly showed the activating role of the solid support in the desired reaction.

Table 5. Comparison of the efficiency of MCM-48 with other well-known supports in synthesis of 14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene.

Entry	Carrier	Amount (g, mol%)	Time (h)	Yield (%)
1	$H_5PW_{10}V_2O_{40}$	0.1 mol%	9	79
2	$H_5PW_{10}V_2O_{40}$	0.5 mol%	1.3	95
3	$H_5PW_{10}V_2O_{40}$	1 mol%	0.5	98
4	MCM-48/$H_5PW_{10}V_2O_{40}$	0.06 g	0.6	95
5	MCM-48/$H_5PW_{10}V_2O_{40}$	0.03 g	1.3	95
6	SBA-15/$H_5PW_{10}V_2O_{40}$	0.03 g	1.5	97
7	MCM-41/$H_5PW_{10}V_2O_{40}$	0.03 g	2.5	75
8	$ZrO_2/H_5PW_{10}V_2O_{40}$	0.03 g	3	60
9	$SiO_2/H_5PW_{10}V_2O_{40}$	0.03 g	4	37

Reactions were carried out as described below table 2. 0.03 g of MCM-48/$H_5PW_{10}V_2O_{40}$ was included 0.0075 g of $H_5PW_{10}V_2O_{40}$. This amount was equal to 0.25 mol% $H_5PW_{10}V_2$ O_{40}

Apparently, besides the surface area, particle size, pore structure, and distribution of the protons in HPAs, nature and interaction of supports with HPAs are very influential on the catalytic activity. Silica as a conventional, cheaply available supporting material has attracted more attention among other supports. It is well-established that physiochemical properties of silica has an important role in the final properties of grafted materials. Clearly, the interaction of HPA with various silicas depends on the type of silica and surface characteristics.

3.5 *Comparing the catalytic activity of solid acid MCM-48/$H_5PW_{10}V_2O_{40}$ with other reported catalysts*

The superiority of the present heterogeneous catalytic system over reported methodologies was studied by comparing the obtained results with those reported previously (table 6). The catalytic activity of catalysts was compared considering mol% of the used catalyst, temperature, reaction time, and percentage yields. Among the examined catalysts, $H_5PW_{10}V_2O_{40}$/MCM-48 was the best. MCM-48 activated the heteropolyacid such that 0.06 g of it (including 0.015 g of $H_5PW_{10}V_2O_{40}$) led to the same results as obtained for 1 mol% of catalyst (including 0.03 g of $H_5PW_{10}V_2O_{40}$) under homogeneous condition. This comparison revealed the reactivity pattern of $H_5PW_{10}V_2O_{40}$/MCM-48 > $H_5PW_{10}V_2O_{40}$ > $SiO_2/H_6P_2W_{18}O_{62}$ > $SiO_2/H_3PW_{12}O_{40}$. Heterogeneous nature and explicit catalytic activity of $H_5PW_{10}V_2O_{40}$/MCM-48 are the two key features of the present protocol. Comparison of the heteropolyacid systems with other introduced catalytic routes, clearly, justified the distinct higher activity of $H_5PW_{10}V_2O_{40}$/MCM-48 compared to other methods in the preparation of of 14-aryl-14H-dibenzo[a,j]xanthenes.

3.6 *Reusability of the catalyst*

Studying recoverability of $H_5PW_{10}V_2O_{40}$/MCM-48 has been one of the most important parameters before recommending it for industrial-scale use. To attain this goal, the recycled catalyst was washed with dichloromethane, activated at 130°C for 5 h, and then

Table 6. Comparison of the efficiency of various reported catalysts in synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes.

Catalyst	Catalyst [mol%] or (g)	Time (h)	Yield (%)	Condition (°C)	Ref.
$H_5PW_{10}V_2O_{40}$	[1]	0.5–0.8	82–98	S. F (100)	This work
MCM-48/$H_5PW_{10}V_2O_{40}$	0.06 g	0.6–1	70–99	S. F (100)	This work
$SiO_2/H_3PW_{12}O_{40}$	0.15 g	0.5–1	84–95	S. F (100)	39
$SiO_2/H_6P_2W_{18}O_{62}$	0.2 g	0.5–1.5	84–96	S. F (100)	39
$NH_4H_2PO_4/SiO_2$	0.1 g	0.1–0.4	73–98	S. F (125)	34
37% BF_3/SiO_2	0.08 g	0.25	82–97	S. F (60)	40
$NaHSO_4/SiO_2$	0.1 g	0.1–0.5	75–98	S. F (110)	41
I_2	[10]	2–5	85–95	S. F (90)	42
Sulphamic acid	[10]	6–12	90–95	S. F (125)	43
H_2SO_4:HOAc	1:4 (v:v)	73	60–90	HOAc (80)	44
$KAl(SO_4)_2.12H_2O$	[50]	3–4	82–91	H_2O (100)	45
Montmorillonite K10	0.3 g	2–4	75–89	S. F (120)	46

S.F. refers to solvent-free condition

subjected to a second run. The recovered catalyst was reused for several times and did not show considerable loss of activity after ten times. Thus, the reaction would be carried out with the recovered and/or fresh catalyst with equal efficacy. Stability of the catalyst was investigated via studying the permanency of the characteristic IR bands of *Keggin* structure at *ca*. 1070–1090, 947–955, 846–890, and 778–784 cm^{-1}.[47] These studies confirmed that the mentioned structure should be intact under the reaction condition reported here.

Reusability studies and high catalytic activity of the recovered heterogeneous catalyst clearly confirmed that the loaded heteropolyacid was firmly bound to the MCM-48 surface. Moreover, spectroscopic analysis proved that the morphology of MCM-48 is retained after several reusing of the supported catalyst, similar to those of pure catalyst (figure 4).[38] Therefore, MCM-48 could be considered as one of the promising materials to adsorb heteropolyacids for the catalytic purposes.

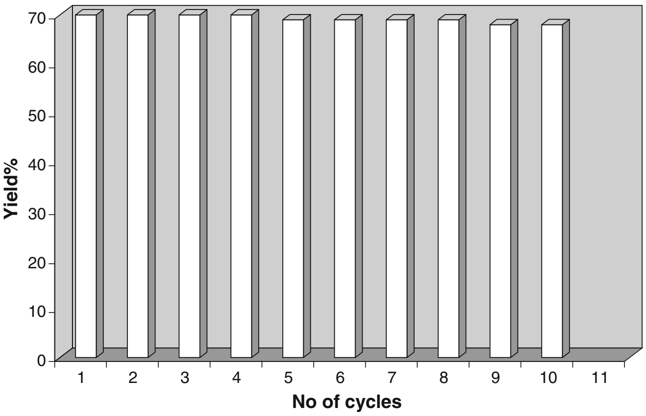


Figure 4. Studying reusability of $H_5PW_{10}V_2O_{40}$/MCM-48 in the three component condensation of 4-nitrobenzaldehyde and β-naphthol after 1 h.

Figure 5 shows the FT-IR spectra of $H_5PW_{10}V_2O_{40}$, MCM-48, and MCM-48/$H_5PW_{10}V_2O_{40}$. The *Keggin*-type heteropolyacid has four characteristic peaks in the range of 750–1100 cm^{-1}.[47] It can be seen that peaks appeared at 778–784 cm^{-1} and 846–890 cm^{-1}

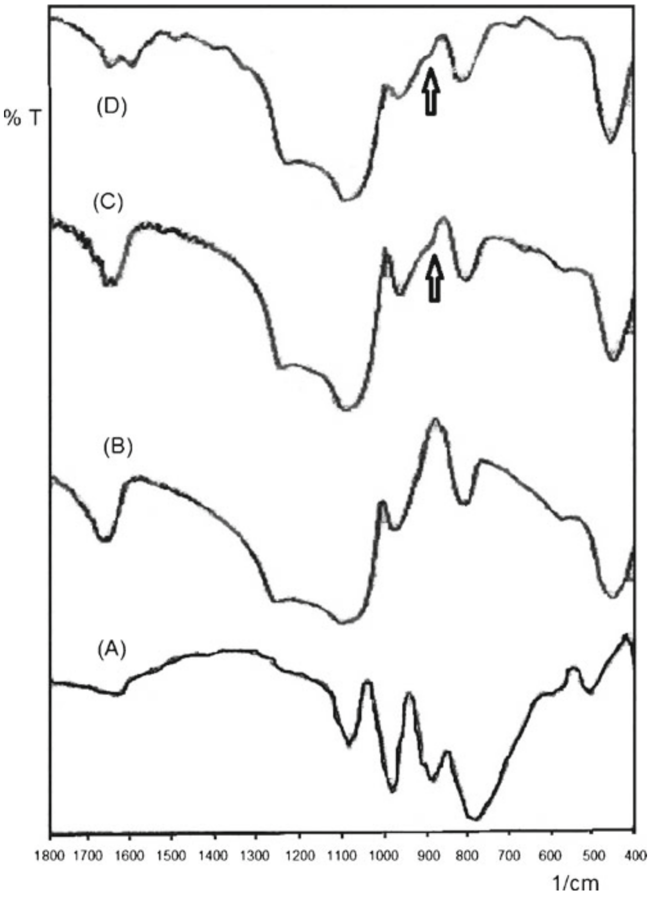
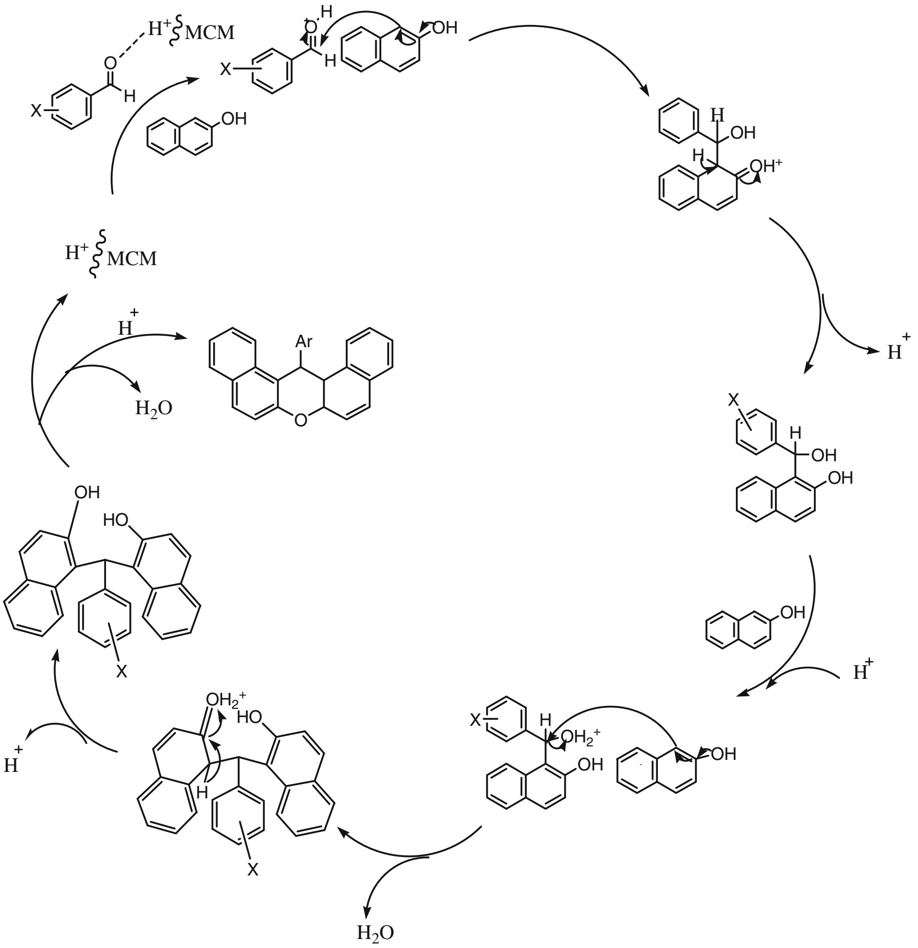


Figure 5. IR spectra of (A) $H_5PW_{10}V_2O_{40}$, (B) MCM-48, (C) MCM-48/$H_5PW_{10}V_2O_{40}$ before reaction, and (D) MCM-48/$H_5PW_{10}V_2O_{40}$ after reaction.



Scheme 2. Suggested reaction pathway for the preparation of 14-aryl-14H-dibenzo[a,j]xanthenes catalysed by $H_5PW_{10}V_2O_{40}$/MCM-48.

correspond to M–O–M and peaks at 947–955 cm^{-1} and 1070–1090 cm^{-1} are related to M=O and P–O, respectively. That explicitly indicates the neat structure of *Keggin*-type heteropolyacid. In FT-IR spectrum of HPW/MCM-48, these peaks overlap with MCM-48, therefore these informations cannot confirm that loading of heteropolyacid was occurred over MCM-48. However, due to appearance of weak new peaks in the FT-IR spectrum of HPW/MCM-48 in range of 850–950 cm^{-1} in comparison with MCM-48, confirmed that HPW actually existed in the pores of MCM-48.

Finally, a reasonable reaction pathway is proposed for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes by means of the heteropolyacid $H_5PW_{10}V_2O_{40}$ immobilized on MCM-48 (scheme 2).[28,30,43]

4. Conclusion

A highly efficient and environmentally friendly protocol is presented for the synthesis of aryl-14H-dibenzo[a,j]xanthenes. Condensation of aromatic aldehydes with β-naphthol in the presence of a catalytic amount of $H_5PW_{10}V_2O_{40}$/MCM-48 under solvent-free conditions led to excellent yields. Low cost, easy work-up, short time, and using mild reaction condition are some advantages of the present protocol.

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