



Single step synthesis of coumarin derivatives over Al-MCM-41 and its supported catalysts under solvent-free condition

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ABSTRACT

Al-MCM-41 (Mobil Composition Mater) (Si/Al=25) molecular sieve was synthesized hydrothermally and 20 and 40 wt% phosphotungstic acid (PW) was supported on it. The materials were characterized using XRD, pyridine adsorbed FT-IR, ^{31}P and ^1H MAS NMR techniques. Catalytic performance of the materials was examined in the liquid phase condensation of resorcinol and ethyl acetoacetate. 7-Hydroxy-4-methylcoumarin was the only product observed in this reaction. The results revealed that 20 wt% PW/Al-MCM-41 is found to be more active than other catalysts. The reaction parameters were optimized to obtain high selectivity of the desired product at maximum resorcinol conversion. The reaction was also performed with substituted phenolic derivatives and ethyl acetoacetate in order to realize the substituent effect.

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1. Introduction

Coumarin and its derivatives have been attracting great interest because they occupy a special place in the realm of natural products and synthetic organic chemistry. Many products, which contain the subunit of coumarin, exhibit useful and diverse biological activity such as molluscicides, anthelmintic, hypnotic, etc. or serve as anticoagulant agents and fluorescent brighteners [1–3]. Coumarin derivatives also find applications in pharmaceutical, fragrance and agrochemical industries [4]. 7-Hydroxy-4-methylcoumarin acts as a starting material in the preparation of hymecromone insecticide. Pechmann reaction is the most widely used method for preparing coumarins since it starts from simple starting materials and offers high yield. Mineral acids like H_2SO_4 , HCl and H_3PO_4 , CF_3COOH and Lewis acids such as ZnCl_2 , FeCl_3 , SnCl_4 , TiCl_4 and AlCl_3 were used as catalysts in the conventional coumarin synthesis [5]. However, this method suffers due to formation of unnecessary by-products, long reaction time and corrosion of equipments. To avoid such problems, there have been efforts to find environmentally benign alternative and heterogeneously catalysed synthetic routes. The use of heterogeneous acid catalysts offers advantages like ease of operation conditions, reduced equipment corrosion and minimized contamination of waste streams combined with

reusability. Nafion-H, zeolite β , Amberlyst 15 and other solid acids have been employed as catalyst in the Pechmann reaction [3,4,6]. Gunnewegh et al. [4] first reported Pechmann condensation of resorcinol and ethyl acetoacetate over zeolite H β in toluene to obtain 7-hydroxy-4-methylcoumarin. In the case of Amberlyst 15, special equipment such as microwave oven was used for accelerating this reaction [7]. Potdar et al. [8] reported the synthesis of 7-hydroxy-4-methylcoumarin over neutral ionic liquids ([bmim] PF_6 / POCl_3) but it required hazardous POCl_3 . Al-MCM-41 (Mobil Composition Mater) with different Si/Al ratios was used as efficient catalysts for a variety of organic reactions [9]. They are economical and harmless catalysts, which can be filtered easily from the reaction mixture and reused. Al-MCM-41 molecular sieves have already been proved to be an effective catalyst for alkylation and acylation reactions [10–12]. The present study describes an ecofriendly procedure for the synthesis of coumarin derivative over Al-MCM-41 (Si/Al=25) and 20 and 40 wt% PW (phosphotungstic acid) supported Al-MCM-41 (Si/Al=25) catalysts under solvent-free condition.

2. Experimental

2.1. Catalyst preparation

All reagents viz., sodium metasilicate, aluminum sulphate, cetyltrimethyl ammonium bromide (CTAB), sulfuric acid, resorcinol and ethyl acetoacetate were purchased from Merck and used

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as such. Hydrothermal crystallization method described by Beck et al. [13] was slightly modified for the preparation of Al-MCM-41 (25). All experimental details and physico-chemical characterization of the catalysts were found to be similar to our earlier report [12]. The preparation procedure and characterization of 20 and 40 wt% PW/Al-MCM-41 alone are described in this article. Catalysts with 20 and 40 wt% loadings of $\text{H}_3\text{PW}_{12}\text{O}_{34}\cdot x\text{H}_2\text{O}$ (PW, E-Merck GR grade, Germany) on Al-MCM-41 (25) were prepared by stirring a suspension of 1.0 g Al-MCM-41 in 10 ml methanol containing either 0.2 or 0.4 g PW at room temperature for 22 h [14]. The resultant mixture was dried at 80 °C and calcined at 200 °C for 2 h. This method facilitated retention of all added PW on the support.

2.2. Analytical methods

The powder X-ray diffraction patterns for Al-MCM-41 (25) and supported catalysts were recorded using a Siemens D5005 Stereoscan diffractometer using a nickel filtered Cu K α radiation (operating at 40 kV and 30 mA) source and a liquid nitrogen-cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range 0.8–10° in steps of 0.02° with a count time of 10 s at each point. Aluminum content in Al-MCM-41 (25) was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with Labtam Plasma 8440 instrument.

The specific surface area and pore properties of Al-MCM-41 were measured by nitrogen physisorption at –196 °C with an ASAP-2010 volumetric adsorption analyzer (Micrometrics Corporation, Norcross, GA, USA). Before nitrogen adsorption–desorption measurements, Al-MCM-41 samples were degassed at 350 °C under a pressure of 10^{-5} Torr overnight. The specific surface area of the samples was determined from the linear portion of BET plots. The pore size distribution was calculated from the desorption branch of N₂ adsorption–desorption isotherms using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP 2010 built-in software from Micromeritics).

FT-IR spectra of the catalysts were recorded using FT-IR spectrometer (Nicolet, Avatar 360) with a resolution of 2 cm⁻¹ and 50 scans. About 15 mg of the sample was pressed (under a pressure of 2 ton/cm²) into a self-supported wafer of 13 mm diameter. This pellet was used to record the infrared spectra in the range 4000–400 cm⁻¹. The acidity of catalysts was determined by in situ DRIFT pyridine adsorption and desorption technique. The in situ DRIFT spectra of the samples were recorded on a FT-IR spectrometer (Nicolet Avatar 360) equipped with a high temperature vacuum chamber. Approximately 10 mg of the sample was taken in the sample holder and dehydrated at 400 °C for 6 h under vacuum (10^{-5} mbar). The sample was then cooled to room temperature. Then pyridine was adsorbed at room temperature. The physically adsorbed pyridine was removed by heating the sample at 150 °C under vacuum (10^{-5} mbar) for 30 min, cooled to room temperature and then recorded the IR spectrum in the range 1700–1400 cm⁻¹ (pyridine adsorption region).

³¹P MAS NMR spectra were recorded using a solid-state NMR spectrometer (Bruker DSX-300) with a magnetic field strength of 7.04 T. The spinning rate was 8 kHz and the resonating frequency was 121.5 MHz. The other parameters were spectral width 8 μ s, recycle delay 2 s and number of transients 1043. Solution of phosphoric acid was used as reference for ³¹P nuclei. ¹H MAS NMR spectra were recorded on a NMR spectrometer Bruker Avance 400 operating at 400 MHz. Zirconia rotor (4 mm outer diameter) was spun at 10 kHz about the magic angle. The spectra were obtained by accumulating 16 scans with $\pi/2$ pulse duration of 10 μ s and rep-

etition time of 8 s. Chemical shifts were measured relative to TMS as external reference.

2.3. Catalytic study

The liquid phase reaction was carried out in a batch reactor consisting of a three-necked round bottom flask fitted with a condenser, a connector for nitrogen purge and a sampling apparatus. The reaction mixture viz., resorcinol (10 mmol), ethyl acetoacetate (20 mmol) and catalyst (0.5 g) was taken in the reactor and heated in an oil bath to the requisite temperature with simultaneous stirring using a magnetic stirrer. Prior to each experiment the empty reactor was purged with nitrogen to remove oxygen in order to avoid oxidation. Aliquots of the reaction mixture were withdrawn at regular intervals and the liquid products were analyzed using a gas chromatograph (Shimadzu GC-17A) with DB-5 capillary column (cross-linked 5% phenylmethyl polysiloxane) (30 m \times 0.25 mm \times 0.25 μ m) equipped with a flame ionization detector (FID). Nitrogen was used as the carrier gas at a flow rate of 20 ml min⁻¹. The products were identified using a PerkinElmer Auto System XL gas chromatograph (PE-5 capillary column, 30 m \times 0.25 mm \times 1 μ m) coupled with mass spectrometer (Turbo)(EI, 70 eV). Helium was used as the carrier gas at a flow rate of 1 ml min⁻¹. The components present in the products were identified from m/e values and mass fragmentation patterns. The resorcinol conversion and selectivity of 7-hydroxy-4-methylcoumarin were calculated using the following equations [11,15]:

$$\text{selectivity of the product (\%)} = \frac{\text{7-hydroxy-4-methylcoumarin (\%)}}{\text{reactants derived products (\%)}} \times 100$$

$$\text{conversion of resorcinol (\%)} = \frac{\text{weight of resorcinol consumed (g)}}{\text{initial weight of resorcinol (g)}} \times 100$$

3. Results and discussion

3.1. Physico-chemical characterization

3.1.1. X-ray diffraction

X-ray powder diffraction patterns of Al-MCM-41 (25) and 20 and 40 wt% PW/Al-MCM-41 (25) are shown in Fig. 1. Al-MCM-41 (25) showed characteristic XRD patterns which are indexed to hexagonal lattice as reported by earlier workers [13,15]. PW/Al-MCM-41 catalysts with 20 and 40 wt% exhibited (1 0 0) plane reflection at 2.32° (2θ) whereas Al-MCM-41 (25) showed at 2.24° (2θ). This indicates decrease in pore size and illustrates maximum use of PW to construct Keggin phase within the pores. However, the intensity of peak decreased upon increasing PW loading and the peaks appeared above 20° (2θ) corresponding to crystalline phase of PW. Comparison of the XRD patterns of pure Al-MCM-41 and PW/Al-MCM-41 revealed that the mesoporous structure is rather intact even after loading of PW. The d_{100} spacing and unit cell parameters (a_0) derived from the XRD of pure Al-MCM-41 (25) and 20 and 40 wt% PW/Al-MCM-41 catalysts are presented in Table 1. The d_{100} spacing is less for PW-loaded catalysts than pure Al-MCM-41. This observation reveals pore size contraction as a result of lining of PW film on the mesoporous channel. The Keggin structure of PW is retained in 20 and 40 wt% PW/Al-MCM-41 [16]. These details are very well reflected from the values of pore diameter and pore volume of PW/Al-MCM-41 catalysts given in Table 2.

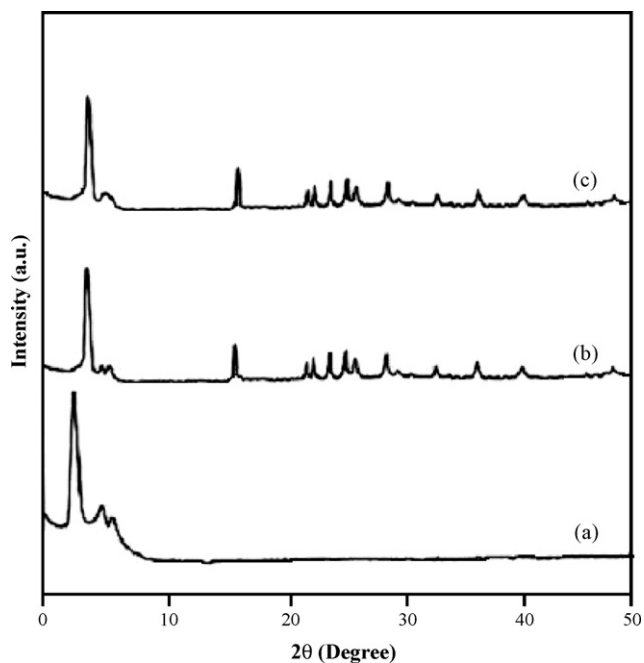


Fig. 1. XRD patterns of (a) Al-MCM-41 (25), (b) 20 wt% PW/Al-MCM-41 and (c) 40 wt% PW/Al-MCM-41.

Table 1

XRD d_{100} spacing and lattice parameter (a_0) values of pure Al-MCM-41 (25) and PW/Al-MCM-41 catalysts

Catalyst	d_{100} (Å)	a_0 (Å)
Al-MCM-41 (25)	40.58	46.91
20 wt% PW/Al-MCM-41	39.47	45.42
40 wt% PW/Al-MCM-41	39.12	45.07

3.1.2. BET analysis of pure Al-MCM-41 and supported Al-MCM-41

Nitrogen adsorption isotherms of Al-MCM-41 (25), 20 and 40 wt% PW/Al-MCM-41 catalysts are shown in Fig. 2a. Each isotherm showed type IV character corresponding to typical shape of mesoporous MCM-41. All materials exhibited a steep rise commencing at ca. $p/p_0 = 0.27$ – 0.32 due to capillary condensation of nitrogen in the mesopores of ca. 2.1–2.5 nm diameter [17]. The specific surface area of the samples ranges between 702 and 902 $\text{m}^2 \text{g}^{-1}$ (Table 2). The decrease of pore diameter observed for 20 and 40 wt% PW/Al-MCM-41 catalysts are in line with our view (Fig. 2b). The decrease in pore volume for PW-loaded catalysts compared to pure Al-MCM-41 evidently proved the formation of PW Keggin phase within the pores of Al-MCM-41. The gradual decrease in pore volume with increase of PW loading also confirmed the formation of Keggin phase within the pores of Al-MCM-41 [18].

3.1.3. ^{31}P MAS NMR spectra of PW/Al-MCM-41

^{31}P MAS NMR is the most reliable method to examine the state of phosphorus in heteropoly acids. ^{31}P MAS NMR spectra of 20 and 40 wt% PW-loaded Al-MCM-41 catalysts are shown in Fig. 3. The PW/Al-MCM-41 catalysts containing 20 and 40 wt% PW exhib-

Table 2

Textural properties of pure Al-MCM-41 (25) and PW/Al-MCM-41 catalysts

Catalyst	BET surface area (m^2/g)	Pore diameter (Å)	Pore volume (cm^3/g)
Al-MCM-41 (25)	902	24.89	0.76
20 wt% PW/Al-MCM-41	790	22.84	0.51
40 wt% PW/Al-MCM-41	702	22.79	0.44

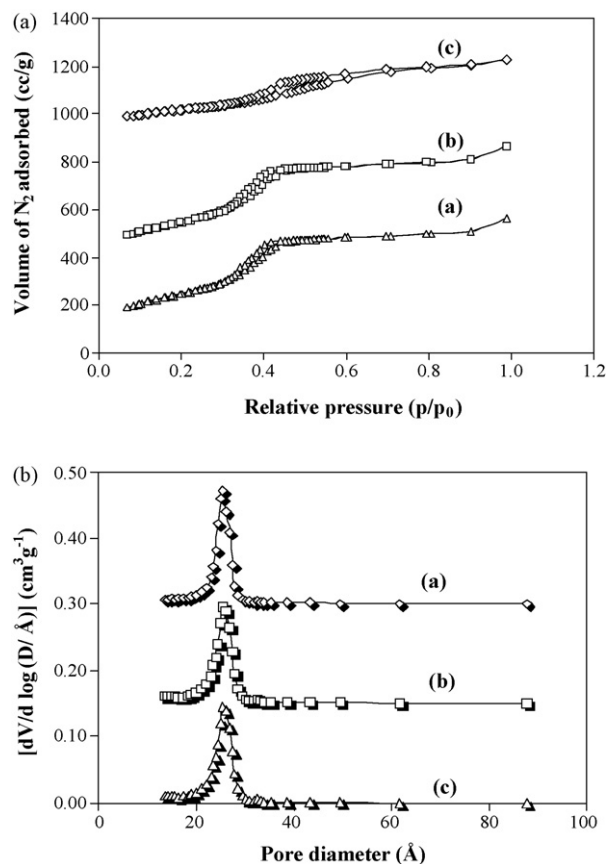


Fig. 2. (a) Adsorption isotherms of (a) Al-MCM-41 (25), (b) 20 wt% PW/Al-MCM-41 and (c) 40 wt% PW/Al-MCM-41, (b) pore size distribution in (a) Al-MCM-41 (25), (b) 20 wt% PW/Al-MCM-41 and (c) 40 wt% PW/Al-MCM-41.

ited a sharp resonance at -15.2 ppm which is close to that of bulk PW [19]. This indicates unambiguously that Keggin structure is retained when PW is loaded on Al-MCM-41. However, the spectrum of PW/Al-MCM-41 with low PW content indicates partial decomposition of Keggin structure due to the formation of species such as $\text{PW}_{11}\text{O}_{39}^{7-}$ and $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ or unsaturated anions like $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ and $\text{P}_2\text{W}_{21}\text{O}_{71}^{6-}$ [19].

3.1.4. ^1H MAS NMR spectra of pure and supported Al-MCM-41

The ^1H MAS NMR spectra of Al-MCM-41 (25) and 20 and 40 wt% PW/Al-MCM-41 catalysts are shown in Fig. 4. The weak signals appeared at 1.1 and 1.5 ppm are assigned to defective Si–OH groups [20]. The intense peak at 4.77 ppm is assigned to Brönsted acid sites [21]. The Gaussian appearance without any shoulder illustrates nearly similar type of Brönsted acid sites on the catalyst surface. This is contrary to the previous reports which states acid sites of different strength on the surface of Al-MCM-41 [11,22]. The leveling of acid strength may be due to low Si/Al ratio of the catalyst. ^1H MAS NMR spectra of 20 and 40 wt% PW/Al-MCM-41 showed intense and sharp signal at 4.77 ppm. This peak appeared very narrow in comparison to Al-MCM-41 thus illustrating nearly the same environment of protons when loaded with PW.

^1H MAS NMR spectrum of PW generally gives a characteristic signal at 9.3 ppm [20,23]. But this signal is absent in the present spectrum and hence the acidity of PW protons is equalized to those of Al-MCM-41. Similar observation has been already reported for PW/MCM-41 [23]. But they have also reported origin of a new signal around 3 ppm due to newly generated protons which is absent in the present spectrum. Hence such protons originated by the modi-

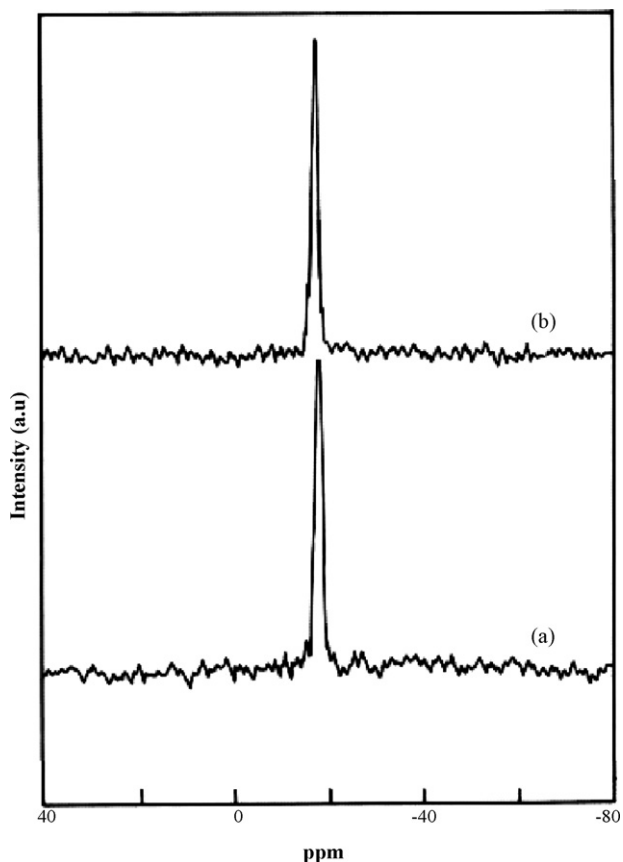


Fig. 3. ^{31}P MAS NMR spectra of (a) 20 wt% PW/Al-MCM-41 and (b) 40 wt% PW/Al-MCM-41.

fication of defective Si–OH groups are not observed in this catalyst. But the signal due to defective sites between 1 and 2 ppm appeared very much resolved compared to Al-MCM-41 catalyst. Hence acidity of some of the defective –OH groups is considered to be modified to Brønsted acid sites that gave signal at 4.77 ppm. Certainly there may be condensation of very close defective –OH groups.

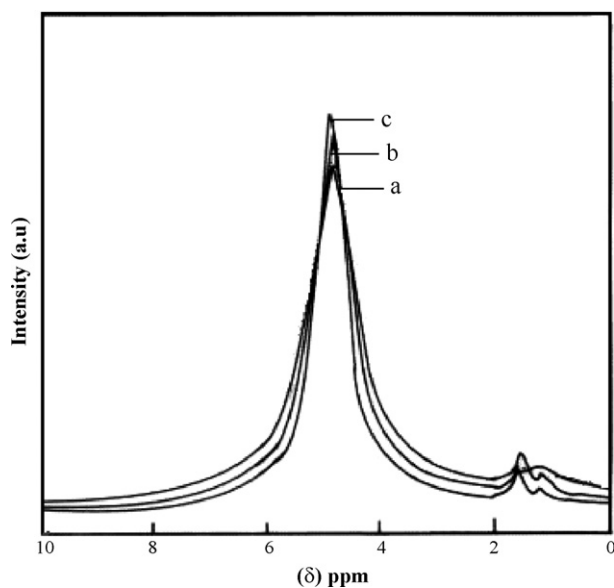


Fig. 4. ^1H MAS NMR spectra of (a) Al-MCM-41 (25), (b) 20 wt% PW/Al-MCM-41 and (c) 40 wt% PW/Al-MCM-41.

Based on these observations it is concluded that PW is not present as a separate entity on the catalyst surface but interacted with Al-MCM-41. Comparison of this spectrum with 20 and 40 wt% PW/Al-MCM-41 illustrated nearly similar features. The important observation in the spectra of PW-loaded catalysts is the increase in the intensity of signal due to defective –OH sites. Hence, there could be breaking of some type of bridges into fresh Si–OH groups. Hence this study unambiguously established crystallization of Keggin phase particularly inside the pores of Al-MCM-41, thus it can be a novel, convenient and effective support for PW. The failure of crystallization outside the pores of Al-MCM-41 therefore illustrates strong interaction between Al-MCM-41 and PW within the pores.

3.1.5. FT-IR spectra of Al-MCM-41 supported PW

FT-IR spectra were recorded for Al-MCM-41 supported PW samples in order to confirm the presence of Keggin anion on the surface of Al-MCM-41. FT-IR spectrum of Al-MCM-41 (25) is also included in Fig. 5 for comparison purpose. The $\text{PW}_{12}\text{O}_{40}^{3-}$ Keggin ion structure consists of a PO_4 tetrahedron surrounded by four W_3O_{13} groups formed by edge sharing octahedra. These groups are connected to each other by corner sharing oxygen. The typical bands of Keggin absorption at 1091, 968 and 802 cm^{-1} are clearly seen in Fig. 5. This structure gives rise to four types of oxygen which is responsible for the finger print bands of Keggin ion between 1200 and 700 cm^{-1} . The bands at 1080 and 984 cm^{-1} correspond to P–O and W=O vibrations, respectively. The corner-shared and edge-shared vibration of W–O–W band occurred at 892 and 800 cm^{-1} , respectively [19]. These spectral features remained the same irrespective of PW loading. It is concluded that significant amount of crystallization of Keggin phase observed at and above 20 wt% loading of PW.

3.1.6. In situ DRIFT spectra of Al-MCM-41 and PW/Al-MCM-41

FT-IR spectra of supported catalysts were recorded after adsorption of pyridine followed by evacuation at elevated temperatures

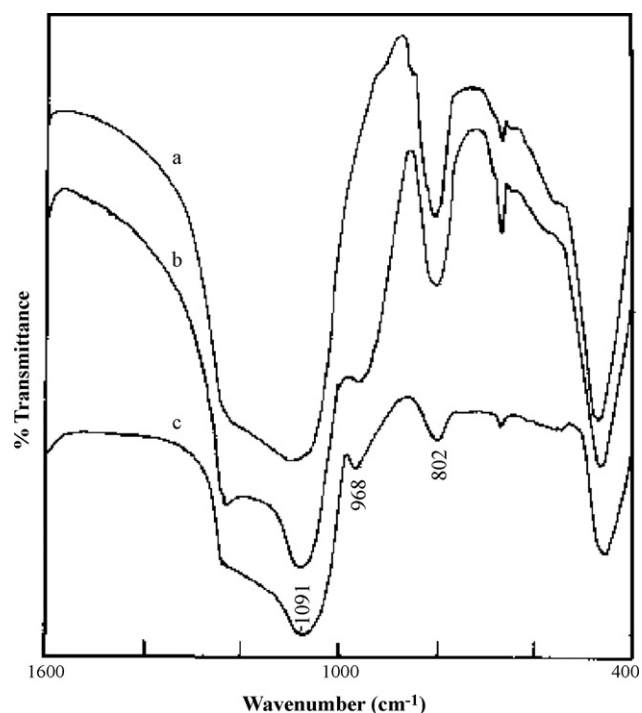


Fig. 5. FT-IR spectra of (a) Al-MCM-41 (25), (b) 20 wt% PW/Al-MCM-41 and (c) 40 wt% PW/Al-MCM-41.

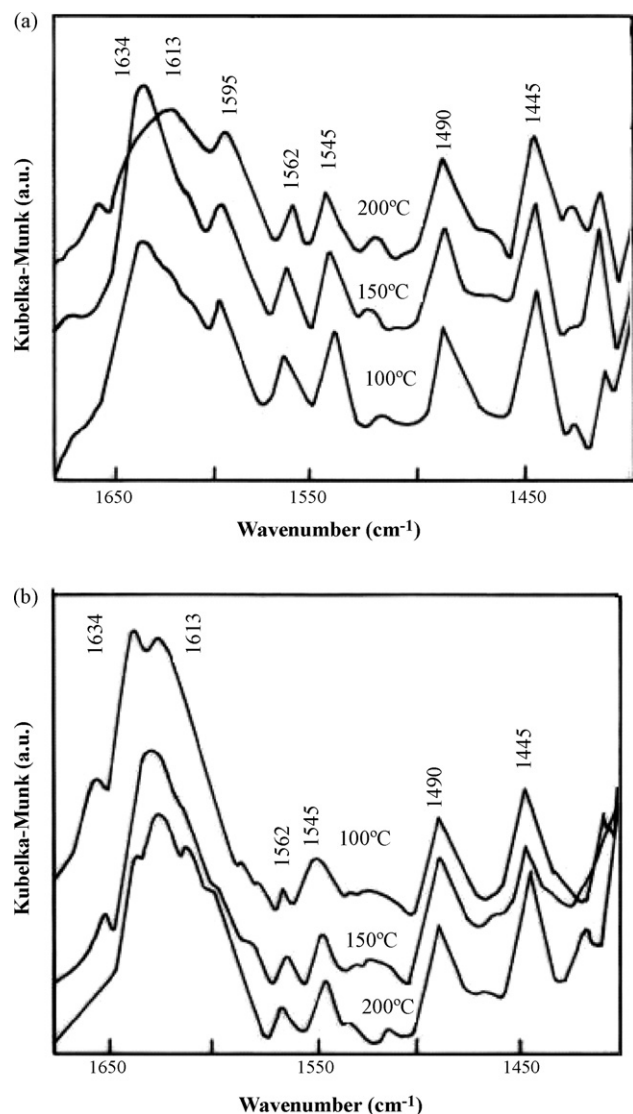


Fig. 6. In situ DRIFT spectra of pyridine adsorbed over (a) 20 wt% PW/Al-MCM-41 and (b) 40 wt% PW/Al-MCM-41.

(Fig. 6a and b). The spectra showed contribution of pyridine adducts in the region 1650–1450 cm^{-1} . The formation of pyridinium ion adsorption at 1545 and 1490 cm^{-1} is characteristic of Brønsted acid sites and both Brønsted and Lewis acid sites, respectively [24].

The band appeared at 1634 cm^{-1} is due to ring vibration of pyridine bound to Brønsted acid sites [21]. The bands at 1445 and 1613 cm^{-1} are assigned to hydrogen-bonded pyridine which is characteristics of Lewis acid sites [11,25]. Comparison of the spectra revealed that 20 wt% PW/Al-MCM-41 possesses greater amount of acid sites (B and L acid sites) than other catalysts as the corresponding bands of 20 wt% PW/Al-MCM-41 are more intense than 40 wt% PW/Al-MCM-41. The intensity of bands at 1613, 1490 and 1445 cm^{-1} reduced at elevated temperatures for all the catalysts but the band at 1545 cm^{-1} remained almost same, particularly in the case of 20 wt% PW/Al-MCM-41 indicating the presence of strong Brønsted acid sites in the catalyst. The decrease of absorption band at 1445 cm^{-1} indicated diminishing nature of physisorbed pyridine after evacuation at elevated temperatures [26].

3.2. Catalytic studies

Intermolecular condensation of resorcinol and ethyl acetoacetate was carried over Al-MCM-41 (25) and Al-MCM-41 (25) supported PW catalysts in the liquid phase. The reaction was also performed by changing the reaction parameters like temperature and reaction time to obtain high yield of the product at maximum conversion. The intermolecular condensation and subsequent intramolecular cyclisation led to the formation of 7-hydroxy-4-methylcoumarin.

3.2.1. Effect of temperature

The influence of temperature viz., 100, 125, 150 and 175 $^{\circ}\text{C}$ on resorcinol conversion and selectivity of 7-hydroxy-4-methylcoumarin was studied over Al-MCM-41 (25) and 20 and 40 wt% PW/Al-MCM-41 with a feed ratio 1:2. The reaction was carried for 4 h and the results are presented in Table 3. The resorcinol conversion increased with increase in temperature up to 150 $^{\circ}\text{C}$ and thereafter it attained steady state over all the catalysts (Fig. 7). There was no significant difference in conversion between 150 and 175 $^{\circ}\text{C}$. The selectivity of 7-hydroxy-4-methylcoumarin also remained above 95% at an optimum temperature of 150 $^{\circ}\text{C}$. 20 wt% PW/Al-MCM-41 (25) gave higher resorcinol conversion than other catalysts but the selectivity of 7-hydroxy-4-methylcoumarin did not show much variation. The selectivity remained between 95 and 98% at all temperatures. The yield of 7-hydroxy-4-methylcoumarin is also shown in the same table. The results indicate almost similar trend as that of Al-MCM-41 catalysts towards conversion and product selectivity. Hence, it could be visualized that the same mechanism prevailed over both the catalysts. But a slight increase in conversion and selectivity of the desired product was observed over 20 wt% PW/Al-MCM-41 compared to Al-MCM-41 at 150 $^{\circ}\text{C}$.

Table 3

Effect of temperature on resorcinol conversion, selectivity and yield of 7-hydroxy-4-methylcoumarin over various catalysts

Catalyst	Temperature ($^{\circ}\text{C}$)	Resorcinol conversion (%)	Selectivity of 7-hydroxy-4-methylcoumarin (%)	Yield of 7-hydroxy-4-methylcoumarin (%)
Al-MCM-41 (25)	100	50.5	94.7	47.8
	125	64.3	99.0	63.7
	150	72.3	97.6	70.6
	175	73.0	97.3	71.0
20 wt% PW/Al-MCM-41(25)	100	61.0	95.6	58.3
	125	70.6	95.0	67.1
	150	80.3	97.8	78.5
	175	80.6	97.8	78.8
40 wt% PW/Al-MCM-41(25)	100	57.8	95.2	55.0
	125	66.2	96.4	63.8
	150	74.5	99.0	73.7
	175	75.0	98.8	74.1

Catalyst amount = 0.5 g; reactants ratio = 1:2 (10 mmol:20 mmol); reaction time = 4 h.

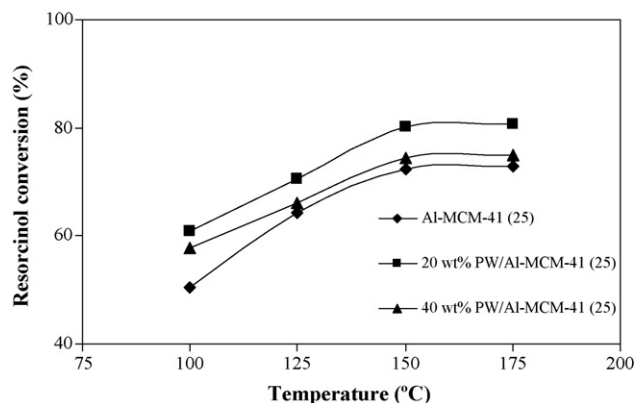


Fig. 7. Effect of temperature on resorcinol conversion over Al-MCM-41 (25), 20 wt% PW/Al-MCM-41 (25) and 40 wt% PW/Al-MCM-41 (25), mole ratio 1:2, time 4 h.

The presence of Keggin structure with high density of acid sites inside the mesopores of Al-MCM-41 may be the reason for the slight increase in conversion and selectivity. 40 wt% PW/Al-MCM-41 gave less conversion than 20 wt% PW/Al-MCM-41 catalysts as high dense Keggin structure could offer diffusional constrain. Such a diffusional constrain was reported by previous workers [27,28]. There is only a slight difference in conversion and selectivity of product over par-

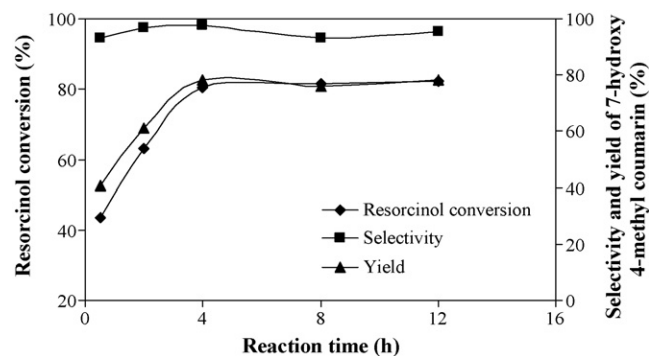
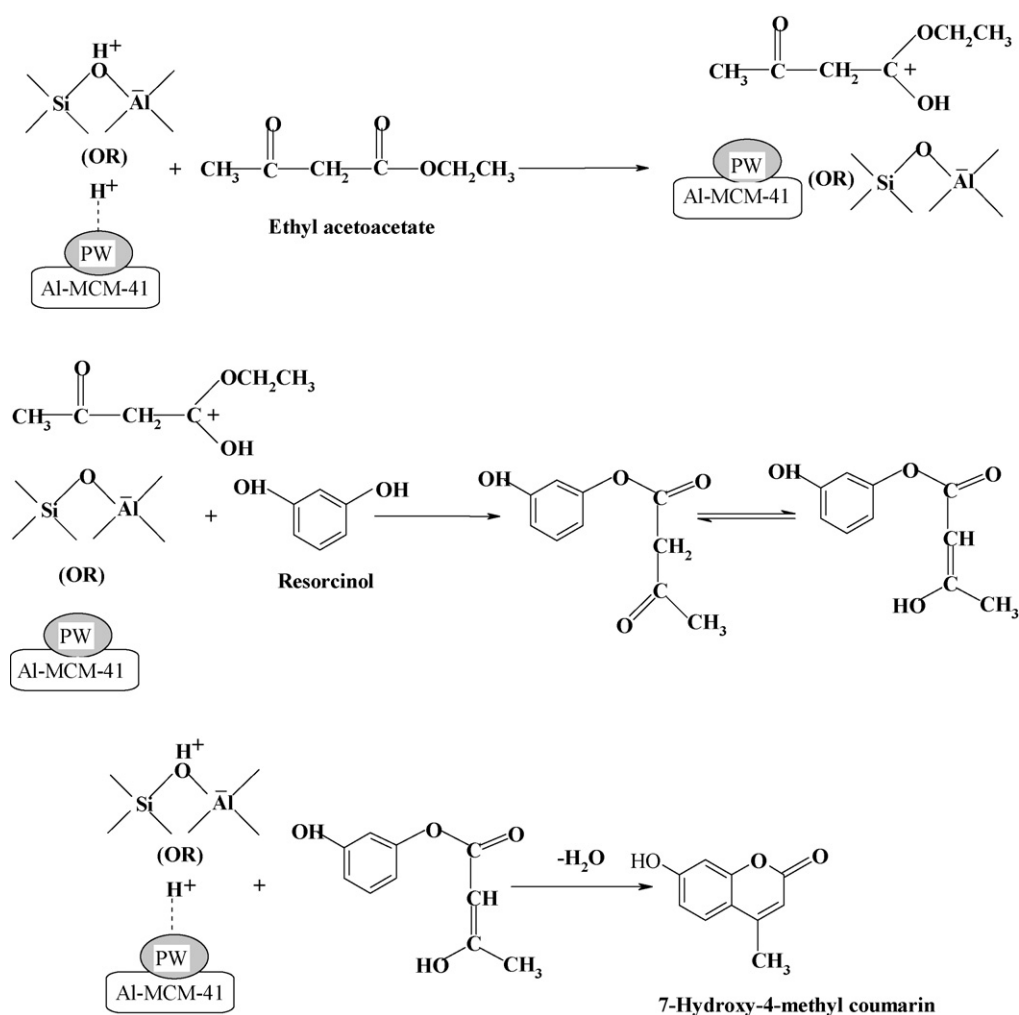


Fig. 8. Effect of reaction time on resorcinol conversion, selectivity and yield of 7-hydroxy-4-methylcoumarin over 20 wt% PW/Al-MCM-41 (25).

ent Al-MCM-41 and PW/Al-MCM-41. Hence, part of the acidity due to PW must be used up in breaking Si–OH–Al bridges of Al-MCM-41 (25). Such destruction of Brönsted acidity was also reported in the literature [29]. The selectivity of 7-hydroxy-4-methylcoumarin was found to be nearly the same over all the catalysts (Fig. 8). The intermediates formed in this reaction are shown in the reaction Scheme 1. The plausible mechanism for the formation of 7-hydroxy-4-methylcoumarin is the chemisorption of carbonyl group of ethyl acetoacetate on the Brönsted acid sites of the catalyst.



Scheme 1. Plausible pathway for the formation of 7-hydroxy-4-methylcoumarin over Al-MCM-41 and PW/Al-MCM-41.

Table 4
Effect of reaction time on resorcinol conversion, selectivity and yield of 7-hydroxy-4-methylcoumarin

Time (h)	Resorcinol conversion (%)	Selectivity of 7-hydroxy-4-methylcoumarin (%)	Yield of 7-hydroxy-4-methylcoumarin (%)
0.5	43.5	93.1	40.5
2	63.0	96.8	61.0
4	80.3	97.6	78.5
8	81.4	93.4	76.0
12	82.1	95.6	78.5

Catalyst amount = 0.5 g; temperature = 150 °C; reactants ratio = 1:2 (10 mmol:20 mmol).

The resorcinol makes a nucleophilic attack on it to give the intermediate which rapidly undergoes cyclisation through intramolecular condensation yielding 7-hydroxy-4-methylcoumarin. This reaction is also catalysed by Brønsted acid sites of the catalysts. Electrophilic reaction of chemisorbed ethyl acetoacetate on resorcinol is ruled out as chromones are not observed in this study.

3.2.2. Effect of reaction time

The reaction was carried out from 0.5 to 12 h over 20 wt% PW/Al-MCM-41 (25). The reaction conditions, resorcinol conversion and selectivity of 7-hydroxy-4-methylcoumarin are presented in Table 4. The conversion increased rapidly with increase in reaction time and attained steady state close to 4 h (Fig. 8). Hence, the time required for high conversion of this condensation reaction may be taken as 4 h. The yield and selectivity of 7-hydroxy-4-methylcoumarin also attained steady state at the end of 4 h. Hence, the optimum conditions for this condensation reaction are temperature 150 °C, reactant ratio 1:2 and reaction time 4 h. There is no other except 7-hydroxy-4-methylcoumarin observed in any part of the reaction. Thus it is presumed that intermolecular condensation of resorcinol and ethyl acetoacetate and subsequent intramolecular cyclisation are found to be fast.

3.2.3. Synthesis of coumarin derivatives with different phenolic substrates

In order to understand the substituent effect, the reaction was performed with several substituted phenolic derivatives with ethyl acetoacetate over 20 wt% PW/Al-MCM-41 (25) and the results are summarized in Table 5. The reaction appeared to be feasible with resorcinol, phenol, *m*-cresol and *p*-cresol. But 2-amino, 2-chloro and 2-nitrophenols did not undergo this reaction. It was already reported that 2-chlorophenol does not undergo this condensation reaction in the presence of Lewis acid such as Zn with iodine [30]. Similarly the condensation reaction with 4-chlorophenol also failed to afford the corresponding coumarin. Thus electron donating group in phenol promoted the reaction while electron withdrawing group inhibited the reaction. The absence of condensation reaction with these substrates may be attributed to the formation of intermolecular hydrogen bonding, which decrease the nucleophilicity of phenolic oxygen could be discerned.

Table 5
Synthesis of coumarin derivatives from various substituted phenols with ethyl acetoacetate over 20 wt% PW/Al-MCM-41

Substrate	Solvent/temperature (°C)	Time (h)	Yield (%)
Resorcinol	None/150	6	79.3
Phenol	None/150	2	55.2
<i>m</i> -Cresol	None/150	8	64.7
<i>p</i> -Cresol	None/150	8	60.5
2-Aminophenol	None/150	12	–
2-Nitrophenol	None/150	12	–
2-Chlorophenol	None/150	12	–

Catalyst amount = 0.5 g; reactants ratio = 1:2 (10 mmol:20 mmol).

4. Conclusion

The results of present investigation concluded that 20 wt% PW/Al-MCM-41 (25) is a convenient substitute for conventional hazardous catalysts for the preparation of 7-hydroxy-4-methylcoumarin with high selectivity at maximum resorcinol conversion. Since the reaction did not form any side product, the targeted main product is not contaminated. The formation of intermediate in the intermolecular condensation prior to intramolecular cyclisation was not observed in this study. In conclusion, it has been demonstrated that Al-MCM-41 and PW/Al-MCM-41 catalysed Pechmann reaction under solvent-free condition is an efficient alternative for the preparation of coumarin derivatives.

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