Arabian Journal of Chemistry (2017) **10**, S757–S764

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Solvent free one-pot multi-component synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones catalyzed by mesoporous $NH_4H_2PO_4$/MCM-41 as an environmentally friendly, cheap, and effective catalyst

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Received 20 August 2011; accepted 1 December 2012
Available online 13 December 2012

KEYWORDS

3,4-Dihydropyrimidin-2(1*H*)-ones;
MCM-41;
Ammonium dihydrogen phosphate

Abstract A green and efficient method is described for the solvent free synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones through one-pot three-component condensation of ethyl acetoacetate, an aryl aldehyde, and urea using mesoporous MCM-41 supported ammonium dihydrogen phosphate ($NH_4H_2PO_4$/MCM-41) as catalyst. The present methodology offers several advantages such as high yields, relatively short reaction times, mild reaction condition, easy work up, and using a highly recyclable catalyst. Some mechanistic studies revealed that the reaction would be achieved via formation of an acyliminium ion, followed by an acid-catalyzed cyclodehydration step.

1. Introduction

3,4-Dihydropyrimidinones (DHPMs) are important biologically active materials, acting as calcium channel antagonists, anti-bacterial, anti-hypertensive, anti-inflammatory agents, and possessing cytotoxic activity (Azizian et al., 2010). Therefore, development of new, efficient, and convenient protocols that lead to substituted DHPMs is of considerable attention. Although, a simple and straightforward multi-component procedure was first established (Biginelli, 1893), significant efforts have been made to find new effective procedures to prepare DHPMs in better yields under milder conditions during the past decade. Numerous optimized procedures have been reported where most of them employed various Lewis acid catalysts such as ionic liquids (Li et al., 2006; Gholap et al., 2004), polymer-supported catalysts (Dondoni and Massi, 2001), and zelolites (Rani et al., 2001). However, most of these methods often require relatively harsh reaction conditions such as high temperatures, expensive or highly acidic catalysts, and

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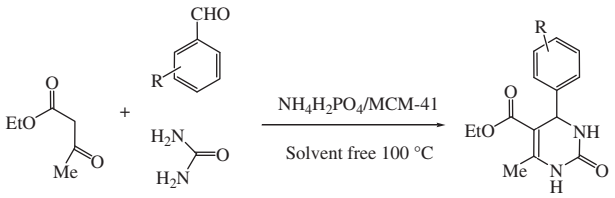
Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2012.12.001



Scheme 1 General formulation for the Biginelli three components condensation of urea, aromatic aldehyde, and ethyl acetoacetate catalyzed by $NH_4H_2PO_4$/MCM-41.

prolonged reaction times. Thus, the development of mild methods using catalysts derived from renewable resources for the synthesis of DHPMs still remains a challenge for organic chemists.

It is of great practical importance to synthesize 3,4-dihydropyrimidin-2(1*H*)-ones using easily separable and reusable solid catalyst having pore size large enough to allow the diffusion of reactant and substrate molecules, requiring short reaction time, particularly without using any solvent. $NH_4H_2PO_4$ is an excellent ammonium surrogate to other catalysts because it is cheap, exhibits high activity and low toxicity. Moreover, $NH_4H_2PO_4$ can be used with considerable advantages such as mild reaction conditions and avoiding of by-products. In continuation of our interest to synthesize dihydropyrimidin-2(1*H*)-ones (Tayebee et al., 2012, 2013), the present study was undertaken for this purpose by using ammonium dihydrogen phosphate supported on mesoporous MCM-41 (Scheme 1).

2. Materials and methods

The used chemicals were purchased from Aldrich and Merck chemical companies. All products were characterized by comparison of their spectral and physical data with those reported in the literature (Zendehdel et al., 2008). Progress of the reactions was monitored by TLC. Infrared spectra were recorded (KBr pellets) on 8400 Shimadzu Fourier Transform spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE instrument using TMS as an internal reference. Data for ^{1}H NMR are reported as 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. Synthesis of MCM-41 support

MCM-41 was re-crystallized from a gel with the molar composition SiO_2:0.29 Na_2O:0.50 C_{14}TMABr:150 H_2O. 9.9 g of sodium silicate solution (8% Na_2O, 27% SiO_2, Merck) was diluted with 30 mL water and was added slowly to a rapidly stirred solution of 7.48 g [$(C_{14}H_{29})NMe_3$]Br in 80 mL H_2O. A precipitate formed immediately which was stirred at ambient temperature for 30 min. To adjust the pH of the gel from 12.0 to 10.0, dilute sulfuric acid (2 M) was then added drop wise. After stirring for further 30 min, the pH was readjusted to 10.0. The mixture was then autoclaved at 100 °C for 2 days in Teflon-lined stainless steel reaction vessels. The solid product was recovered by filtration, washed with hot water and air-dried at 60 °C. Finally, calcination was carried out at 540 °C for 6 h (Nunes et al., 2002).

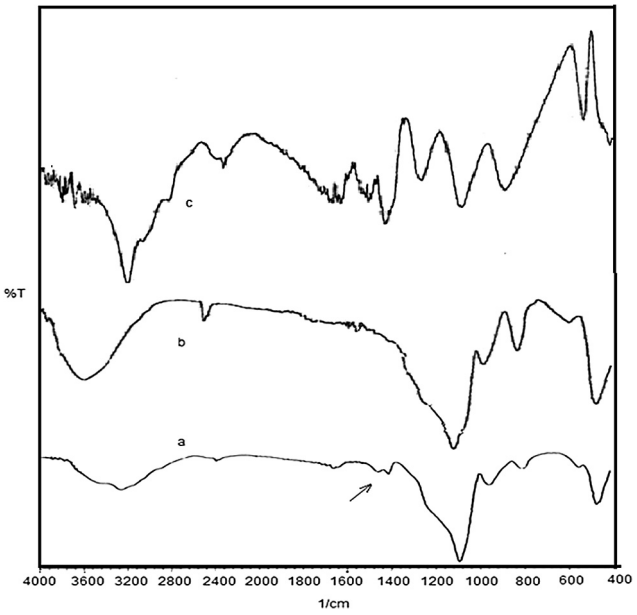


Figure 1 Infrared spectra of (a) $NH_4H_2PO_4$/MCM-41; (b) MCM-41 and; (c) $NH_4H_2PO_4$.

2.2. Preparation of $NH_4H_2PO_4$/MCM-41

The catalyst was prepared by mixing MCM-41 (1.5 g) with a solution of $NH_4H_2PO_4$ (0.6 g) in distilled water (10 ml). The resulting mixture was stirred for 12 h to absorb $NH_4H_2PO_4$ on the surface of MCM-41. After removing water, the solid powder was dried at 120 °C for 12 h. The drying temperature was maintained below the decomposition temperature of the ammonium salt (Mahdavinia et al., 2009). Infrared spectra of free and supported catalysts are shown in Fig. 1.

2.3. General procedure for the preparation of 3,4-dihdropyrimidin-2(1H)-ones

A solution of ethyl acetoacetate (0.26 g, 2 mmol), aldehyde (2 mmol) and urea (2.5 mmol) was heated to 100 °C under solvent-free condition in the presence of $NH_4H_2PO_4$/MCM-41 (0.04 g). Progress of the reaction was monitored by TLC. At the end of the reaction, the resulting mixture was filtered and the heterogeneous catalyst was separated. Then, the filtrate was poured into cold water and the solid product was separated by filtration. The impure product, if necessary, was recrystallized from *n*-hexane/ethyl acetate (3:1).

2.4. Spectral data of some selected compounds

2.4.1. Ethyl-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate

FT-IR (KBr, cm^{-1}): 3238, 3113, 2980, 1724, 1649, 1465, 1290. ^{1}HNMR (DMSO-d_6), δ (ppm): 1.09 (t, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.99 (q, 2H, CH_2), 5.13 (d, 1H, H-4), 7.21–7.34 (m, 5H, H_{arom}), 7.73 (s, 1H, NH), 9.19 (s, 1H, NH). ^{13}CNMR (DMSO-d_6), δ (ppm): 14.5, 18.2, 54.5, 59.7, 99.8, 126.7, 127.7, 128.8, 145.3, 148.8, 152.8, 165.8.

2.4.2. Ethyl-6-methyl-4-(2-chlorophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

FT-IR (KBr, cm^{-1}): 3354, 3236, 3111, 2978, 1693, 1641, 1226, 1095. ^{1}HNMR (DMSO-d_6), δ (ppm): 0.99 (t, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.90 (q, 2H, CH_2), 5.63 (d, 1H, H-4), 7.25–7.41 (m, 4H, H_{arom}), 7.71 (s, 1H, NH), 9.27 (s, 1H, NH). ^{13}CNMR (DMSO-d_6), δ (ppm): 14.4, 18.1, 51.9, 59.5, 98.3, 128.2, 129.2, 129.5, 129.8, 132.1, 142.2, 149.8, 151.8, 165.4.

2.4.3. Ethyl-6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

FT-IR (KBr, cm^{-1}): 3215, 1731, 1707, 1641; ^{1}HNMR (DMSO-d_6), δ (ppm): 1.07 (3H, t, 3 J 6.8 Hz, CH_3), 2.26 (3H, s, CH_3), 3.97 (2H, q, 3 J 5.4 Hz, OCH_2), 5.27 (1H, s, CH), 7.50 (2H, d, 3 J 7.3 Hz, H_{arom}), 7.87 (1H, s, NH), 8.20 (2H, d, 3 J 7.2 Hz, H_{arom}), 9.33 (1H, s, NH). ^{13}CNMR (DMSO-d^6), δ (ppm): 14.5, 18.3, 54.2, 59.8, 98.7, 124.2, 128.1, 147.2, 149.8, 152.2, 152.5, 165.5.

2.4.4. Ethyl-6-methyl-4-(4-methylphenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

FT-IR (KBr, cm^{-1}): 3326, 3152, 1691, 1562, 1232, 1051, 783; ^{1}HNMR (DMSO-d_6), δ (ppm): 1.12 (t, J = 7.5 Hz, 3H), 2.28, 2.30 (s, 3H), 4.00 (q, J = 7.5 Hz, 2H), 5.11 (d, J = 3.0 Hz, 1H), 7.25 (m, 4H), 7.70 (br s, 1H, NH), 9.19 (br s, 1H, NH).

2.4.5. Ethyl-6-methyl-4-(3-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

FT-IR (KBr, cm^{-1}): 3300, 3120, 1710, 1690, 1630; ^{1}HNMR (DMSO-d_6), δ (ppm): 1.11 (t, J = 7.5 Hz, 3H), 2.29 (s, 3H), 4.02 (q, J = 7.5 Hz, 2H), 5.31 (d, J = 3.0 Hz, 1H), 7.65–7.75 (m, 2H), 7.95 (br s, 1H), 8.09–8.20 (m, 2H), 9.34 (br s, 1H).

2.4.6. Ethyl-6-methyl-4-(4-chlorophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate

FT-IR (KBr, cm^{-1}): 3220, 3100, 1720, 1700; ^{1}HNMR (DMSO-d_6), δ (ppm): 1.10 (t, J = 7.2, 3H), 22 (s, 3H), 3.96 (q, J = 7.2, 2H), 5.02 (s, J = 3.2, 1H), 6.64 (d, J = 8.4, 2H), 7.02 (d, J = 8.4, 2H), 7.57 (s, 1H), 9.07 (s, 1H).

3. Results and discussion

Although, homogeneous catalytic systems find widespread applications in the chemical industry, nevertheless, several drawbacks such as intractability of separation from products, difficulty of recovery and recycling, generation of acidic wastes, and low product selectivity limited their applications. In contrast, immobilized catalysts could remove these problems and thus, maximize their importance for academia and industrial catalysis. Even though, the catalytic applications of silica supported reagents for organic synthesis have been established and solid-supported reagents have gained considerable interest in organic synthesis, to the best of our knowledge, there is no report on the use of $NH_4H_2PO_4$ supported on MCM-41 mesoporous silica for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones.

Initially 4-nitrobenzaldehyde, ethyl acetoacetate, and urea were chosen as model substrates to optimize the reaction conditions. Stirring the above mixture in the presence of 0.04 g of $NH_4H_2PO_4$/MCM-41 (involving 5 mol% $NH_4H_2PO_4$) at 100 °C for 2.5 h afforded the expected dihydropyrimidone in a satisfactory yield (85%).

Table 1 Effect of $NH_4H_2PO_4$/MCM-41 amount on the Biginelli reaction under solvent free condition.

Entry	$NH_4H_2PO_4$/MCM-41 amount (g)	NH_4H_2PO (mol%)	Time (h)	Yield (%)
1	0	0	9	54 (Impure)
2	0.02	2.5	3.5	77
3	0.04	5	2.5	85
4	0.08	10	2.4	88

Reaction condition: 4-nitrobenzaldehyde (2 mmol), ethyl acetoacetate (2 mmol), urea (2.5 mmol), 100 °C.

In order to fine-tune the reaction conditions, the effect of catalyst amount (Table 1) and reaction temperature (Table 2) were optimized carefully. The efficiency of the reaction is mainly affected by the amount of the catalyst. Simple heating of a neat mixture of aldehyde, acetoacetate, and urea at 100 °C under solvent free condition in the absence of catalyst led to fair yields and only a highly impure product obtained after 9 h (Table 1, entry 1); while good results were afforded in the presence of $NH_4H_2PO_4$/MCM-41. 0.02 g of the heterogeneous catalyst produced 77% of the product after 3.5 h (entry 2). The optimum amount of the catalyst was 0.04 g and higher amount of catalyst did not improve the yield% considerably. This was due to the fact that beyond a certain concentration, more catalyst sites exist than that required by the reactant molecules and, hence, the additional amount of catalyst does not increase the rate of the reaction.

The effect of temperature on the reaction progress was also studied (Table 2). Obtained results showed that the reaction time was obviously reduced with increasing temperature. Higher temperatures, above 100 °C, had no important effect on the yield% and only decreased the reaction time. Therefore, considering technical points of view, the temperature 100 °C was selected for all reactions. Enhancing temperature above 120 °C had no much influence on the yield% and reaction time.

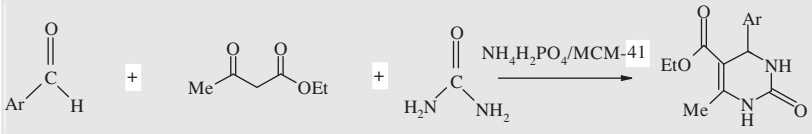
In order to evaluate the generality of this methodology, a range of 3,4-dihydropyrimidin-2(1*H*)-ones were prepared under the optimized reaction conditions (Table 3). Aromatic, heterocyclic and aliphatic aldehydes underwent a smooth transformation into the corresponding 3,4-dihydropyrimidin-2(1*H*)-ones in satisfactory yields. In all cases, aromatic aldehydes with substituents carrying electron-withdrawing groups reacted faster than electron-donating substituents and successfully produced the expected products in good yields and excellent selectivities. Strong electron withdrawing substituent,

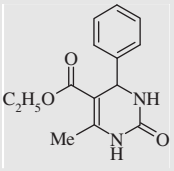
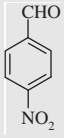
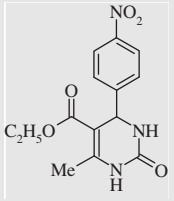
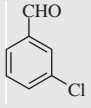
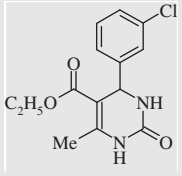
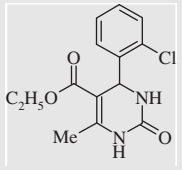
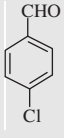
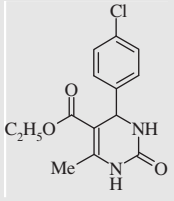
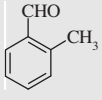
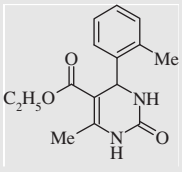
Table 2 Effect of reaction temperature on the three components condensation of 4-nitrobenzaldehyde with ethyl acetoacetate and urea.

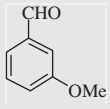
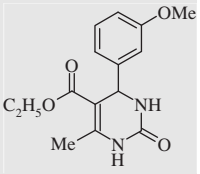
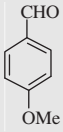
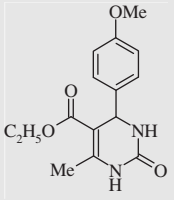
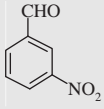
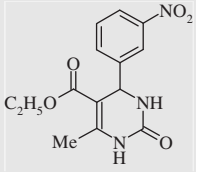
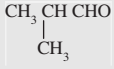
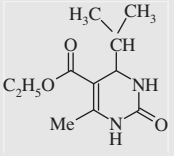
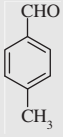
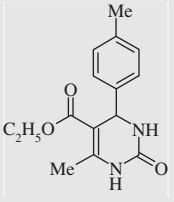
Entry	Temperature (°C)	Time (h)	Yield (%)
1	80	5.2	66
2	100	2.5	85
3	120	1.3	87

Reaction condition is described below Table 1. 0.04 g of catalyst was used in each case.

Table 3 Solvent-free three components condensation of ethyl acetoacetate, urea, and different aldehydes catalyzed by $NH_4H_2PO_4$/MCM-41.



Entry	Aldehyde	Time(h)	Yield (%)	MP mp/lit. mp (°C)	Product
1		6	72	201/201–203 Shaabani and Bazgir (2004)	
2		2.5	85	203–204/205–207 Gangadasu et al. (2004)	
3		5	58	192–194/193–195 Lu et al. (2000)	
4		4.75	89	220–222/222–223 Fu et al. (2002)	
5		3.66	72	208–210/209–211 Gangadasu et al. (2004)	
6		5	47	208–209/208–210 Lu et al. (2000)	

7		6.5	66	207–209/207–208 Ranu et al. (2000)	
8		5	68	200–202/202–204 Lu et al. (2000)	
9		5	70	227/227–228 Mitra and Banerjee (2003)	
10		5	16	194/194–195 Ma et al. (2000)	
11		5	57	212–215/212–214 Hazarkhani and Karimi (2004)	

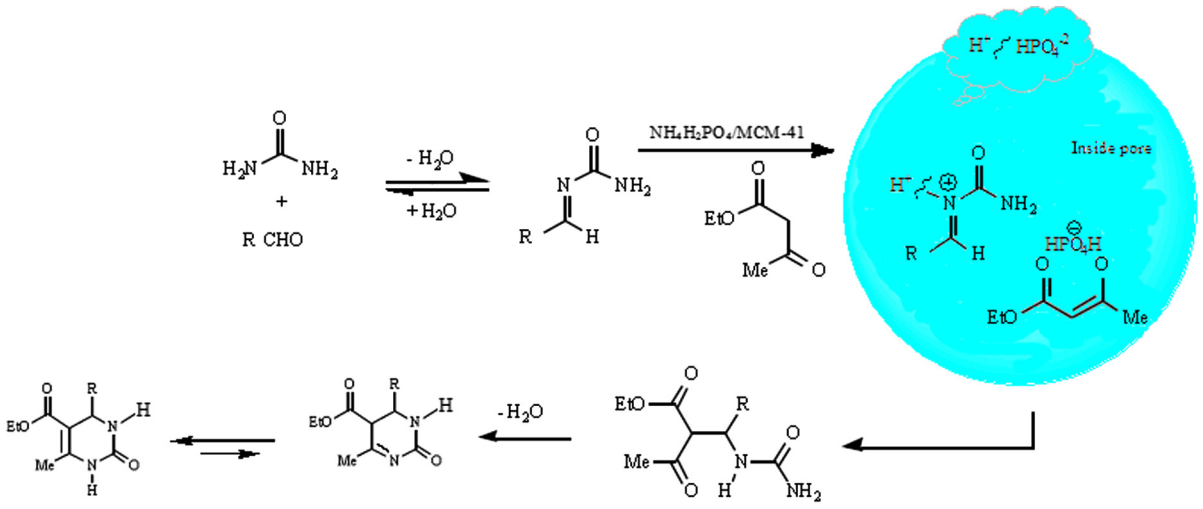
Reaction condition is described below Table 1.

Table 4 Condensation of 4-nitrobenzaldehyde, ethyl acetoacetate, and urea in the presence of $NH_4H_2PO_4$ supported on different solid materials.

Entry	Catalyst	Catalyst amount (g)	Time (h)	Yield (%)
1	$NH_4H_2PO_4$/MCM-41	0.040	2.5	85
2	$NH_4H_2PO_4$/MCM-48	0.040	4.4	74
3	$NH_4H_2PO_4/SiO_2$	0.040	5.6	76
4	$NH_4H_2PO_4$/SBA-15	0.040	3.5	80
5	$NH_4H_2PO_4/ZrO_2$	0.040	3.3	77

Reaction condition is described below Table 1. In all cases 0.011 g of $NH_4H_2PO_4$ was used for 0.029 g of the supporting materials.

–NO_2, distinctly increased the reactivity of aldehyde toward the condensation reaction and led to 85% of product after 2.5 h (entry 2); whereas, benzaldehyde produced 72% of conversion after 6 h (entry 1). Noteworthy, the nitro group on the *meta*-position, slightly affected the reactivity of aldehyde toward the condensation reaction. Chlorinated benzaldehydes showed the reactivity pattern of 2-Cl > 4-Cl > 3-Cl. This reactivity pattern confirmed the role of electronic effects on the reaction progress. Electron donating methyl substituent on the *ortho*-position decreased the efficacy of the reaction and only 47% was obtained



Scheme 2

Table 5 Comparison of the catalytic activity of $NH_4H_2PO_4$/MCM-41 with some other catalysts.

Entry	Catalyst	Catalyst amount (mol%)	Time (h)	Yield (%)	Ref.
1	$Al(H_2O)_6(BF_4)_3$	10	20	81	Litvić et al. (2010)
2	$NiCl_2{\cdot}6H_2O$	10	20	73	Lu and Bai (2002)
3	$CeCl_3{\cdot}7H_2O$	10	20	64	Bose et al. (2003)
4	$ZnCl_2$	10	20	52	Sun et al. (2004)
5	$NH_4H_2PO_4$/MCM-41	5	6	72	This work
6	$CuSO_4{\cdot}5H_2O$	10	24	69	Gohain et al. (2004)
7	$Mn(OAc)_3{\cdot}2H_2O$	10	24	70	Kumar et al. (2001)

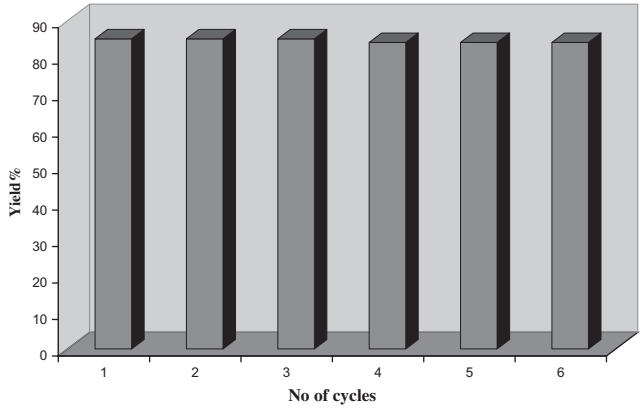


Figure 2 Studying reusability of $NH_4H_2PO_4$/MCM-41 on the three components condensation of 4-nitrobenzaldehyde with ethyl acetoacetate and urea.

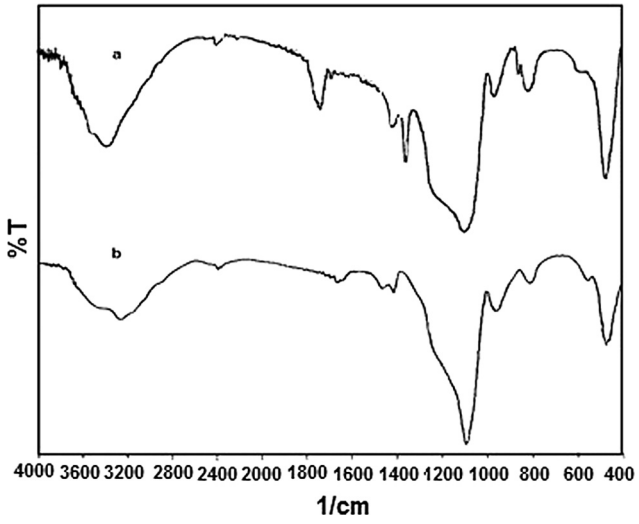


Figure 3 IR spectra of (a) recycled and (b) new $NH_4H_2PO_4$/MCM-41.

after 5 h compared to unsubstituted aldehyde (entry 6). Furthermore, aromatic aldehydes afforded higher yields of the desired products rather than aliphatic aldehydes. Reduced yields of 3,4-dihydropyrimidin-2(1*H*)-ones obtained with aliphatic aldehydes may be attributed to their lower boiling points.

To investigate the effect of supporting material on the efficacy of the reaction, $NH_4H_2PO_4$ was supported on different mesoporous molecular sieves. MCM-41 is a class of mesoporous silica tube-like materials with a hexagonal arrangement of uniformly sized unidimensional mesopores. SBA-15 as a mesoporous silica molecular sieve, has uniform channels and narrow pore size distributions and high surface area. MCM-48 has uniformly sized one dimensional mesopores and has been considered as an ideal support for various organic and inorganic reagents.

According to the obtained results in Table 4, $NH_4H_2PO_4$ supported on MCM-41 showed the best catalytic activity considering reaction time and yield%. MCM-41 clearly behaved better than MCM-48 and commercial silicon dioxide as supporting materials and led to 85% conversion after 2.5 h (entry 1) with respect to 74% obtained after 4.5 h for MCM-48 (entry 2) and 76% obtained for SiO_2 after 5.6 h (entry 3). SBA-15 and ZrO_2 showed moderate efficiency and produced 77–80% conversion after 3.3–3.5 h. These experiments interestingly confirm the effect of supporting material structure on its reactivity.

3.1. Proposed reaction pathway for the synthesis of 3,4-dihydropyrimidinones catalyzed by $NH_4H_2PO_4$/MCM-41

Three theoretical routes are possible for the synthesis of 3,4-dihydropyrimidinones. These routes are Knoevenagel mechanism, iminium mechanism and enamine mechanism (Lal et al., 2012). In order to find out the plausible route for the synthesis of dihydropyrimidinones in the presence of MCM-41/$NH_4H_2PO_4$, three sets of reactions were carried out. First, ethyl acetoacetate was treated with benzaldehyde and was further treated with urea under solvent free conditions in the presence of heterogeneous $NH_4H_2PO_4$. The reaction failed and the desired product was not formed. Secondly, benzaldehyde was treated with urea yielded Schiff base/iminium ion which was then treated with ethyl acetoacetate under solvent free conditions in the presence of catalyst. Finally, ethyl acetoacetate was treated with urea, enamine product was formed, which was then treated with benzaldehyde in the presence of catalyst, the desired product was not formed. Therefore, it may be concluded that the second route using iminium route is the most possible for the synthesis of 3,4-dihydropyrimidinone in the presence of $NH_4H_2PO_4$/MCM-41. According to the above findings, a proposed mechanism depicted in Scheme 2 is adapted for the desired Biginelli reaction catalyzed by $NH_4H_2PO_4$/MCM-41. The mechanism includes the acid-catalyzed formation of C–N bond from benzaldehyde and urea and formation of acyliminium ion, followed by acid-catalyzed addition of β-ketoester to the aryl(or alkyl)idene–urea and cyclodehydration of intermediates yielding the desired dihydropyrimidinone (Folkers and Johnson, 1933; Sweet and Fissekis, 1973; Kappe, 1997). $NH_4H_2PO_4$ might promote the reaction by accelerating the formation of C–N bond and formation of the acyliminium ion and addition reaction through a metal enolate formation or coordination to an acyliminium ion.

Catalytic activity of $NH_4H_2PO_4$/MCM-41 has been compared with some other catalysts published before in the synthesis of 5-ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one. $NH_4H_2PO_4$/MCM-41 catalytic system reacted faster by using lower amounts of catalyst compared to other protocols (Table 5).

3.2. Recycling and reusing of $NH_4H_2PO_4$/MCM-41

One of the most important features of the present methodology is the recyclability of the catalyst. It was observed that the supported catalyst could be reused (Fig. 2). For this purpose, the same model reaction was again studied under the optimized conditions. After completion of the first run, the reaction mixture was dissolved in hot methanol, the solid catalyst was separated by filtration, dried at 100 °C for 2 h, and reused for the same reaction process. Results revealed that the recycled catalyst behaved as the new one and no significant decrease either in yield% or selectivity was observed. FT-IR spectra of the catalysts before and after recycling are depicted in Fig. 3.

4. Conclusions

An efficient, mild, and green methodology has been developed for the synthesis of dihydropyrimidin-2(1*H*)-ones through one-pot three-component reaction of ethyl acetoacetate, aryl aldehyde, and urea under solvent free condition using the heterogeneous $NH_4H_2PO_4$/MCM-41 catalyst. The catalyst could be reused after a simple work-up and used several times without noticeable reduction in the catalytic activity. Good to excellent yields, relatively short reaction times, simple operation and easy work-up are some advantages of this protocol. This improved reaction condition allows the preparation of a wide variety of substituted dihydropyrimidinones in high yields and excellent purity under mild reaction conditions. We believe the applicability of $NH_4H_2PO_4$/MCM-41 with the mentioned advantages makes our method superior among other reported methods to synthesize 3,4-dihydropyrimidin-2(1*H*)-ones.

Acknowledgment

The authors are grateful to Vahid Tayebee for critical reading of this manuscript.

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