

FULL PAPER

A Simple and Green Protocol for the Synthesis of 3,4-dihydropyrimidin-2(1H)-ones Using 11-Molybdo-1-vanadophosphoric Acid as a Catalyst Under Ultrasound Irradiation

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Abstract:

A one-pot three-component reaction of ethyl acetoacetate, aldehydes and urea has efficiently been carried out in the presence of 11-molybdo-1-vanadophosphoric acid in ethanol at room temperature under ultrasound irradiation to form the corresponding 3,4-dihydropyrimidin 2(1H)-ones in high yields. The 11-molybdo-1-vanadophosphoric acid ($H_4PMo_{11}V_1O_{40}$) was prepared and characterized by FT-IR spectroscopy, TG-DTA analysis and XRD analysis techniques. The presence of Keggin structure and incorporation of vanadium into the Keggin structure of synthesized $H_4PMo_{11}V_1O_{40}$ catalyst was confirmed by FT-IR and powder XRD analysis techniques. TG-DTA analysis results indicated that $H_4PMo_{11}V_1O_{40}$ catalyst was thermally stable up to the temperature 434 °C. The present catalytic system is recyclable and can be reused without greater loss of reactivity.

Keywords: 3,4-dihydropyrimidin-2(1H)-ones; heteropoly acids; 11-molybdo-1-vanadophosphoric acid; ultrasound irradiation

1. Introduction

Heteropoly acids (HPAs) are complex proton acids that exhibit a wide range of molecular sizes, compositions, and molecular architectures [1]. HPAs are widely used as homogeneous and heterogeneous acid and oxidation catalysts due to their high thermal stability, strong acidity and strong oxidizing ability [2]. Among various HPA structural classes, the Keggin-type HPAs are the most studied class within polyoxometalates, because of their unique properties such as well-defined structure, Bronsted acidity, possibility to modify their acid-base and redox properties by changing their counter-cations, heteroatoms and framework polyatoms [3,4]. Nowadays, catalysis by HPAs is a potential area due to their high catalytic activities and reactivity, ease of handling, allow cleaner reactions in comparison to

conventional catalysts, non-toxicity and experimental simplicity and hence they are generally recognized as clean, safe and green catalysts [5].

Ultrasound irradiation has been considered as an environmentally benign approach which is being used more and more in organic synthesis during the last three decades [6]. A large number of organic reactions can be carried out in higher yields, shorter reaction time and milder conditions under ultrasound irradiation [7]. Moreover, this method is more convenient and can be easily controlled as compared to traditional methods [8].

3,4-Dihydropyrimidin-2-(1H)-ones (DHPMs) are reported to be physiologically and pharmacologically important class of heterocyclic compounds because of their diversified activities such as calcium channel blockers,

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antihypertensive agents, alpha-la-antagonists, anti-inflammatory and antitumor actions [9-11]. They are also found in many natural products for which their synthesis has attracted considerable attention in recent years. These DHPMs were synthesized via Biginelli reaction involving three-component cyclocondensation of ethyl acetoacetate, an aromatic aldehyde and urea under strongly acidic conditions [12]. Recently, several improved methods have been developed for the synthesis of DHPMs using various catalysts such as cadmium sulfate [13], cuprous chloride [14], ionic liquids [cmmim][BF₄] and [bmim][BF₄] [11], rhizopus oryzae lipase biocatalyst [15], Eaton's reagent [16], ionic liquid {[Et₃N-SO₃H]Cl} [17], γ -Fe₂O₃@HAp-Ni²⁺ nanoparticles [18], sodium tertiary butoxide [19], Fe-Al/clay [20], phosphotungstic acid [21], silica sulfuric acid [22], zeolite [23], and Bismuth (III) sulfate trihydrate [24]. However, in spite of their potential utility, many of these reported protocols suffer from certain drawbacks such as prolonged reaction times, poor yields, and harsh reaction conditions, use of toxic and highly acidic catalysts. These shortcomings surely insist for a safe, eco-friendly and efficient method for the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones.

In the present work, we describe the preparation of 11-molybdo-1-vanadophosphoric acid using etherate method and its characterization by FT-IR spectroscopy, TG-DTA analysis and XRD analysis techniques. The prepared 11-molybdo-1-vanadophosphoric acid catalyst was applied for the synthesis of 3,4-dihydropyrimidin 2(1*H*)-one derivatives by one-pot three-component reaction of ethyl acetoacetate, aldehydes and urea under ultrasound irradiation.

2. Results and Discussion

3.1. Characterization of 11-molybdo-1-vanadophosphoric acid H₄[PMo₁₁V₁O₄₀] 30H₂O

The H₄PMo₁₁V₁O₄₀ catalyst was characterized using FT-IR spectroscopic analysis, TGA analysis and powder XRD analysis techniques to confirm Keggin structure and incorporation of vanadium into the Keggin structure.

3.1.1. FT-IR Analysis

Fig.1 shows the FT-IR spectrum of H₄PMo₁₁V₁O₄₀ catalyst. The primary structure of H₄PMo₁₁V₁O₄₀ was confirmed by four characteristic FT-IR bands located between 800 and 1100 cm⁻¹. The characteristic IR bands of H₄PMo₁₁V₁O₄₀ catalyst were appeared at 1065 cm⁻¹ (P-O stretching), 964 cm⁻¹ (M=O stretching), 870 cm⁻¹ (inter-octahedral M-O-M stretching) and 780 cm⁻¹ (intra-octahedral M-O-M stretching). These characteristic bands are regarded as experimental evidences for the existence of the Keggin-type HPAs molecule. Furthermore, these FT-IR characteristic peaks of synthesized catalyst exactly matched with the characteristic IR bands of H₄PMo₁₁V₁O₄₀ acid mentioned in the literature [26].

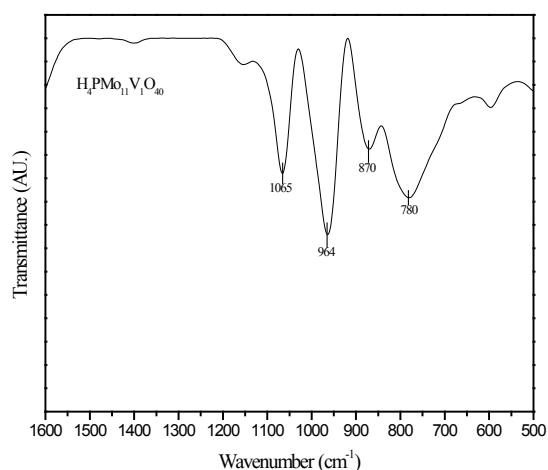


Figure 1. FT-IR Spectrum of H₄PMo₁₁V₁O₄₀ Catalyst

3.1.2. TG-DTA Analysis

The thermal stability of the H₄PMo₁₁V₁O₄₀ catalyst was examined by TG-DTA analysis and the TG-DTA graphs are depicted in Fig. 2 (a) and 2 (b). The initial weight loss of about 11.6% in the TGA data of H₄PMo₁₁V₁O₄₀ up to a temperature of 120 °C corresponds to the loss of free and adsorbed water. A gradual mass loss of about 2.7% up to 450 °C, which was attributed to the decomposition of Keggin units and to the evolution of protonic water, the so-called constitution water.

Fig. 2 (b) shows the DTA curve of H₄PMo₁₁V₁O₄₀ catalyst. Between 40 and 125 °C, DTA shows that all the water molecules do not play the same role. In this temperature range, endothermic peaks due to the presence of water molecules interacting in different ways were

observed. At 434 °C, exothermic peak is observed which is attributed to the decomposition of compound in a mixture of anhydride oxide [26].

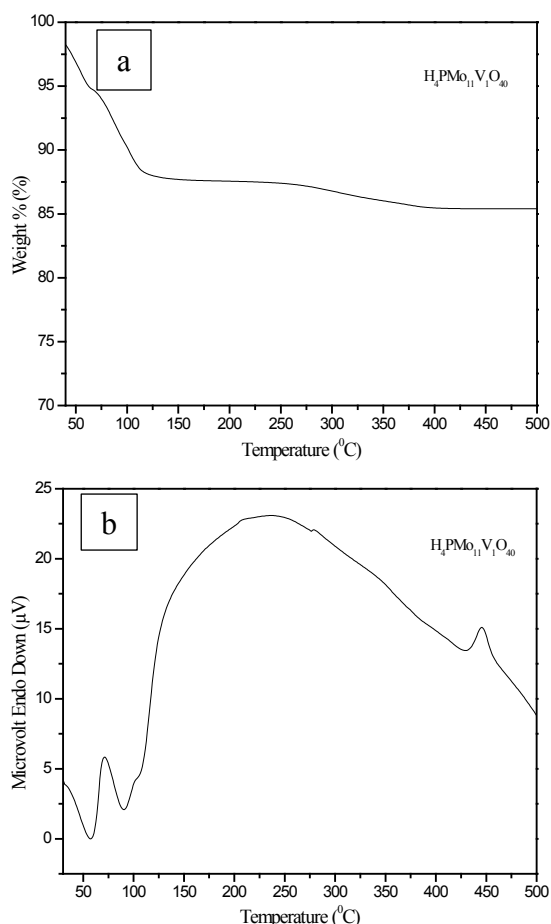


Figure 2. (a) Thermo Gravimetric Analysis of $H_4PMo_{11}V_1O_{40}$ Catalyst. (b) Differential Thermal Analysis of $H_4PMo_{11}V_1O_{40}$ Catalyst

The above TG - DTA results strongly supports that $H_4PMo_{11}V_1O_{40}$ catalyst was thermally stable up to the temperature 434 °C.

3.1.3. Powder XRD Analysis

As shown in Fig. 3, the X-ray diffraction pattern of the $H_4PMo_{11}V_1O_{40}$ catalyst was distributed in four ranges of 2θ , which are 6° - 12° , 16° - 23° and 25° - 30° , revealing that the synthesized $H_4PMo_{11}V_1O_{40}$ catalyst belong to the Keggin-type HPAs [27,28]. XRD pattern of $H_4PMo_{11}V_1O_{40}$ catalyst reflects its secondary structure, which strongly depends upon its environments. The variation in the intensities should be due to the replacement of framework molybdenum by

vanadium and the hydration.

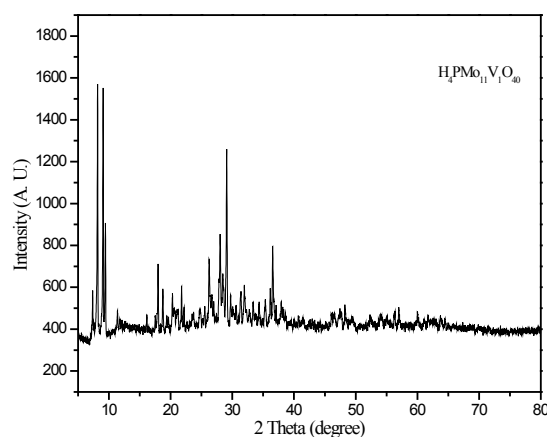


Figure 3. XRD pattern of $H_4PMo_{11}V_1O_{40}$ Catalyst.

3.2. Characterization of selected 3,4-dihydropyrimidin-2(1H)-one derivatives

5-Ethoxycarbonyl-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidine-2-(1H)one (**3c**, Table 3) m.p.: 210-212 °C (lit. [8] m.p.: 212-214°C); 1H NMR ($CDCl_3$, 300 MHz, Me_4Si) δ (ppm): 1.17 (t, 3H, $J = 7.2$ Hz, OCH_2CH_3), 2.34 (s, 3H, CH_3), 4.12 (q, 2H, $J = 7.2$ Hz, OCH_2CH_3), 5.38 (d, 1H, $J = 2.7$ Hz, -CH), 5.73 (s, 1H, NH), 7.23-7.30 (m, 4H, ArH), 7.81 (s, 1H, NH); ^{13}C NMR ($CDCl_3$, 75 MHz, Me_4Si): 14.39, 19.01, 55.42, 60.40, 101.43, 128.24, 129.12, 134.01, 142.40, 146.53, 165.64; MS (EI): m/z 295 (M^+).

5-Ethoxycarbonyl-6-methyl-4-(3,4,5-trimethoxyphenyl)-3,4-dihydropyrimidine-2-(1H)one (**3g**, Table 3) m.p.: 174-176 °C (lit. [11] m.p.: 178-180°C); 1H NMR ($CDCl_3$, 300 MHz, Me_4Si) δ (ppm): 1.19 (t, 3H, $J = 6.9$ Hz, OCH_2CH_3), 2.34 (s, 3H, CH_3), 3.82 (s, 9H, Ar- OCH_3), 4.11 (q, 2H, $J = 7.8$ Hz, OCH_2CH_3), 5.36 (d, 1H, $J = 2.7$ Hz, -CH), 5.88 (s, 1H, NH), 6.53 (s, 2H, ArH), 8.24 (s, 1H, NH); ^{13}C NMR ($CDCl_3$, 75 MHz, Me_4Si): 14.44, 18.85, 56.35, 61.00, 101.50, 103.87, 106.99, 138.02, 139.53, 146.37, 153.60, 153.87, 165.89, 191.27; MS (EI): m/z 350 (M^+).

5-Ethoxycarbonyl-6-methyl-4-(2-thiophenyl)-3,4-dihydropyrimidine-2-(1H)one (**3k**, Table 3) m.p.: 210-212 °C (lit. [11] m.p.: 213-215°C); 1H NMR ($CDCl_3$, 300 MHz, Me_4Si) δ (ppm): 1.24 (t, 3H, $J = 7.2$ Hz, OCH_2CH_3), 2.34 (s, 3H, CH_3), 4.14 (q, 2H, $J = 7.2$ Hz, OCH_2CH_3), 5.70 (s, 1H, -CH), 6.91 (s, 1H, NH), 6.96 (s, 1H, NH), 7.07-7.26 (m, 3H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, Me_4Si): 14.44, 18.98, 51.07, 60.48, 62.15, 102.09, 124.24, 125.17,

126.97, 128.14, 132.58, 134.33, 135.46, 146.61, 147.44, 153.20, 165.51; MS (EI): m/z 266 (M^+)

3.3. Catalytic activity

To find out the suitable conditions for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones, a series of experiments were performed with the standard reaction of benzaldehyde (1 mmol), ethylacetoacetate (1 mmol) and urea (1.5 mmol) in presence of $H_4PMo_{11}V_1O_{40}$ as a model reaction. At the onset study, we try to optimize the model reaction mentioned above by detecting the efficiency of several classic solvents chosen as the medium for comparison under ultrasonic irradiation or without ultrasonic irradiation. Among

the tested solvents such as toluene, dichloromethane, acetonitrile, ethanol, methanol and water the formation of product was more facile and proceeded to give not only in high yield but also with high reaction rate in ethanol (93 yield in 25 min) under ultrasonic irradiation (**Table 1, entry 4**). In order to verify the effect of ultrasound irradiation, the reaction was also performed in mentioned solvents by high stirring alone under silent condition (**Table 1**). As shown in **Table 1**, in all cases, the experimental results show that the yields of the products are lower than sonication and required higher reaction times. Based on the results of this study, it's clear that the ultrasonic technique represented a better procedure in terms of time and yields.

Table 1. Screening of solvents for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones.

Entry	Solvent	Under US irradiation ^a		Without US irradiation ^b	
		Time (min)	Yield ^c (%)	Time (min)	Yield ^c (%)
1	Toluene	25	36	60	22
2	Dichloromethane	25	68	60	38
3	Acetonitrile	25	80	60	52
4	Ethanol	25	93	60	64
5	Methanol	25	85	60	58
6	Water	25	45	60	28

^aReaction of Ethylacetoacetate (1 mmol), aromatic aldehyde (1 mmol) and urea (1.5 mmol) in presence of $H_4PMo_{11}V_1O_{40}$ (0.1 g) under ultrasonic waves for 25 min. ^bReaction of Ethylacetoacetate (1 mmol), aromatic aldehyde (1 mmol) and urea (1.5 mmol) in presence of $H_4PMo_{11}V_1O_{40}$ (0.1 g) under high stirring silent conditions for 60 min. ^cIsolated yield.

In order to optimize concentration of $H_4PMo_{11}V_1O_{40}$, the model reaction was carried out under sonication using different concentration of $H_4PMo_{11}V_1O_{40}$ (**Table 2**). It was found that the best results were obtained with 0.10 g of the $H_4PMo_{11}V_1O_{40}$ catalyst (yield = 93%) under ultrasonic irradiation (**Table 2, entry 6**). Using lower amount of catalyst resulted in lower yields, while higher amount of catalyst did not affect the reaction times and yields and in the absence of catalyst, the yield of the product was not found.

After optimization of the reaction conditions, we studied the reaction of ethylacetoacetate and urea with various aldehydes in presence of $H_4PMo_{11}V_1O_{40}$ catalyst. The results are summarized in **Table 3**. Several aromatic aldehydes with either electron-donating or electron-withdrawing groups attached to the aromatic ring reacted smoothly and the desired

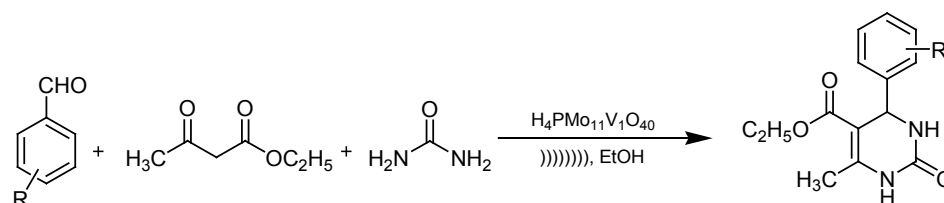
products were obtained in good to excellent yields.

A plausible mechanism for this transformation is proposed in **Fig. 4**.

Table 2. Screening of catalyst concentration on the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones.

Entry	Amount of catalyst (g)	Yield (%) ^b
01	Without catalyst	No reaction
02	0.020	38
03	0.040	52
04	0.060	66
05	0.080	82
06	0.100	93
07	1.120	93

Reaction conditions: Ethylacetoacetate (1 mmol), aromatic aldehyde (1 mmol) and urea (1.5 mmol) in presence of $H_4PMo_{11}V_1O_{40}$ under ultrasonic waves for 25 min. ^bIsolated yield.

Table 3. Synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones using $H_4[PMo_{11}V_1O_{40}] \cdot 30H_2O$ as a catalyst.

Entry	Aldehyde	Product	Time (min)	Yield (%) ^a	Melting point (°C)		Reference
					Found	Reported	
1		3a	25	93	198-200	202-204	8
2		3b	21	95	218-220	216-218	16
3		3c	22	90	210-212	212-214	8
4		3d	20	93	176-178	174-176	11
5		3e	27	92	223-225	228-230	11
6		3f	26	88	179-181	187-189	8
7		3g	28	90	174-176	178-180	11
8		3h	19	94	204-206	207-208	13
9		3i	42	89	222-224	229-231	8
10		3j	16	96	196-198	215-217	13
11		3k	23	93	210-212	213-215	11

Reaction conditions: Ethylacetoacetate (1 mmol), aromatic aldehyde (1 mmol), urea (1.5 mmol) and $H_4[PMo_{11}V_1O_{40}]$ (0.1 g) in ethanol under ultrasonic irradiation. ^aIsolated yield.

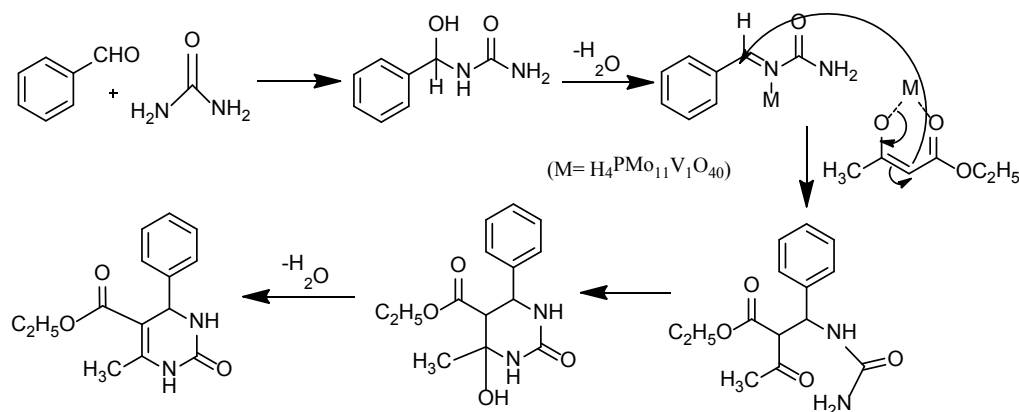


Figure 4. Proposed mechanism for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones.

3.4. Recyclability of the catalyst

The reusability of the catalyst was checked by separating the H₄PMo₁₁V₁O₄₀ catalyst from the reaction mixture by simple filtration and drying in a vacuum oven at room temperature for 4 h followed by drying at 120 °C in an air oven prior to reuse. As a typical example, the catalyst H₄PMo₁₁V₁O₄₀ showed conversion of 90% in the first run, which decreased to about 86% in the 2nd run and 81% in the 3rd run respectively.

3. Material and Methods

2.1. Characterization Techniques

FT-IR spectra were obtained with a Bruker, Germany (Model 3000 Hyperion microscope with vertex 80 FT-IR system) spectrometer. XRD patterns were obtained with a Philips X'pert MPD System instrument using Cu K α radiation. The TG-DTA measurements of the samples were made with the Thermal Analyzer (Perkin Elmer, Model Diamond TG-DTA) with about 10 mg of sample in a platinum crucible at a heating rate of 10 °C min⁻¹ in an air atmosphere. ¹H NMR spectra were recorded on a Bruker Avance 400 and ¹³C NMR were recorded on a Bruker DRX-300 instrument using TMS as an internal reference. Mass spectra were recorded on Waters UPLC-TQD Mass spectrometer using electrospray ionization technique. The uncorrected melting points of compounds were taken in an open capillary in a paraffin bath.

2.2. Preparation of 11-molybdo-1-vanadophosphoric acid H₄[PMo₁₁V₁O₄₀] 30H₂O

Na₂HPO₄ (7.1 g, 0.050 mol) was dissolved in water (100 mL) and mixed with sodium metavanadate (6.1 g, 0.050 mol) that had been dissolved by boiling in water (100 mL). The mixture was cooled and acidified to a red colour with concentrated sulphuric acid (5 mL). To this mixture was added a solution of Na₂MoO₄ · 2H₂O (133 g, 0.55 mol) dissolved in water (200 mL). Finally, concentrated sulphuric acid (85 mL) was added slowly with vigorous stirring of the solution. With this addition the dark red colour changed to lighter red. The heteropoly acid was then extracted with diethyl ether (400 mL) after the water solution was cooled. In this extraction the heteropoly etherate was present in the middle layer; the aqueous layer (bottom) was yellow and probably contained vanadyl species. After separation, a stream of air was passed through the heteropoly etherate layer to free it of diethyl ether. The orange solid that remained was dissolved in water (50 mL), concentrated to the first appearance of crystals in a vacuum desiccator over concentrated sulphuric acid, and then allowed to crystallize further. The orange crystals that formed were filtered, washed with water, and air-dried (28 g, 23%). The amount of water of crystallization varied slightly from sample to sample [25].

2.3. General procedure for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones using H₄[PMo₁₁V₁O₄₀] 30H₂O as a catalyst

A mixture of aromatic aldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), urea (1.5 mmol) and H₄PMo₁₁V₁O₄₀ (0.1 g) was dissolved in minimum quantity of ethanol with constant stirring.

Further the reaction mass was irradiated under ultrasonic irradiation at room temperature for appropriate time, as shown in Table 4.2.3. After completion of the reaction as indicated by TLC, the crude product was washed with ice-cold water and stirred well. The catalyst is soluble in water and was separated from the reaction mixture. The solid obtained was recrystallized from hot ethanol to afford the corresponding pure product.

4. Conclusions

In summary, this article describes preparation of vanadium substituted Keggin-type 11-molybdo-1-vanadophosphoric acid ($H_4PMo_{11}V_1O_{40}$) and its characterization using FT-IR, TG-DTA and Powder XRD techniques. The FT-IR and powder XRD analysis techniques confirm presence of Keggin structure and the vanadium incorporation into the Keggin structure of $H_4PMo_{11}V_1O_{40}$ catalyst. TG - DTA results suggest that $H_4PMo_{11}V_1O_{40}$ catalysts were thermally stable up to the temperature 434 °C. It was demonstrated here that $H_4PMo_{11}V_1O_{40}$ catalyzed one-pot three-component reaction of ethyl acetoacetate, aldehydes and urea under ultrasound irradiation provides an efficient, mild, clean and inexpensive route to obtain 3,4-dihydropyrimidin 2(1H)-ones. The protocol developed using $H_4PMo_{11}V_1O_{40}$ catalyst offers several advantages, including shorter reaction times, easy work-up, low toxicity and reusability of catalyst and it obeys the green chemistry conditions. We believe that this method is a useful and attractive alternative to the existing methods for the synthesis of 3,4-dihydropyrimidin 2(1H)-ones.

Acknowledgments

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