Effect of Poly(ethylene glycol)-400 and Carbon on MoO_3 Nanocomposite Materials and Its Catalytic Activity for Biginelli Reactions

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The effect of addition of poly(ethylene glycol)-400 (PEG-400) and carbon (0, 1, 2 and 3 wt%) as substrates were investigated systematically to get the desired phase of carbon-doped MoO_3 material. The carbon source was prepared from the *Acacia arabica* plant wood. The resulting samples were calcined at 500 ℃. The effect of PEG-400 and carbon composite on the structure, particle size and morphology were investigated. The prepared samples were characterized by XRD, SEM-EDS and FT-IR techniques. The samples with PEG-400 and carbon addition give better control of particle size and porosity. The prepared catalysts were tested for the synthesis of 3,4-dihydropyrimidones via the Biginelli-type condensation reaction. This new method consistently has the advantage of excellent yields (88%—93%) and short reaction times (1.5—3 h) than do classical Biginelli reaction conditions.

Keywords carbon substrate, MoO_3, PEG, Biginelli reaction, 3,4-dihydropyrimidones

Introduction

Acid-catalysed organic reactions are numerous and the usage of solid acid catalysts is very important in several industrial and environmental processes.[1-5] It can be said that solid acids are the most important heterogeneous catalysts used today, considering in terms of both the total amounts used and the final economic impact.[6]

It clearly indicates the significance of these materials and the scope of their commercial exploitation. The use of conventional liquid acids and Lewis acids has significant risks in handling, containment, disposal and regeneration due to their toxic and corrosive nature. Thus, there is need in the development of strong solid acid catalysts which must be stable, regenerable and active at moderate temperatures. Over the past few years, the preparation and characterization of Molybdenum based solid acids has been receiving much attention, among other solid acids such as clays, zeolites, heteropolyacids and ion exchange resins, due to their superior catalytic activity for hydrocarbon conversions.[7-9] Among these nanostructured metal oxides MoO_3, a wide band gap *n*-type semiconductor, is particularly interesting due to their potential applications. It has been extensively investigated as a key material for fundamental research and technological applications in optical devices, smart windows, catalysts, sensors, lubricants, electrochemical storage batteries, information displays and optical filters. Molybdenum oxides and molybdenum oxide based materials are of great technical interest.[10-14]

The Biginelli reaction is one of the most important multi-component reactions for the synthesis of dihydropyrimidinones. Dihydropyrimidinones are known to exhibit a wide range of biological and therapeutic activities such as antiviral, antitumor, antibacterial, and anti-inflammatory, analgesic, blood platelets aggregation inhibitors, cardiovascular properties.[15] The classical Biginelli reaction requires long reaction times (20 h) and often suffers from low yields of products in case of substituted aromatic and aliphatic aldehydes.[16] Multi-step synthesis[17] produces somewhat higher yields but lacks the simplicity of original one-pot Biginelli protocol, hence the Biginelli reaction continues to attract the attention of organic chemists interested in finding milder and more efficient procedures for the synthesis of dihydropyrimidinones. Recently several methods have been reported for preparing dihydropyrimidines using different Lewis acids such as BF_3 OEt_2, $LaCl_3$, $Yb(OTf)_3$,[18-20] as well as protic acids such as H_2SO_4, HOAc, conc. HCl[21-23] as promoters. Many other methods including microwave irradiations, ionic liquids and clay[24] are also reported. However, many of these methods are associated with expensive and toxic reagents, stoichiometric amount of catalyst, reaction time, unsatisfactory yields, incompatibility with other functional groups and involve difficult product isolation procedures. Moreover, some of the methods are practical for aromatic aldehydes only.[25] Thus, there is still a need for

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Received May 6, 2011; revised June 11, 2011; accepted June 21, 2011.

a simple and general procedure for one pot synthesis of dihydropyrimidinone and thiones under mild conditions. Although these methods each have their own merits, they also suffer from the drawbacks with respect to reaction time, cost of reagent and reaction work-ups.

Generally, small surface areas of the resulting catalysts have attracted chemists to seek alternative preparation methods, which allow better control of the structure, size, and morphology of the metal oxides. In this study, a new additive using poly(ethylene glycol) (PEG) was introduced. The PEG is water soluble organic polymer having structure $HO(CH_2OCH_2)_nOH$ (molecular weight ranging from 200 to 10000 g/mol). The effect of PEG-400 (molecular weight around 400 g/mol) addition on morphology of the molybdenum oxide was studied. The improved desired properties of MoO_3 by addition of carbon substrate were explained by the high adsorption of the impurities on the surface of added carbon and their transfer to MoO_3 surface. The carbon substrate were prepared and utilized from natural sources of *Acacia arabica* plant. This study describes a parametric design to determine the effect of PEG and natural carbon obtained from *Acacia arabica* plant on morphology of the molybdenum oxide calcined at 500 ℃.

In this article we reports the improvement in desired properties of MoO_3 by addition of PEG-400 substrate which was explained by the better control of the structure, size, and morphology. Similarly, addition of carbon also explains by high adsorption of the impurities on the surface of added carbon and their transfer to MoO_3 surface. The carbon substrate was prepared and utilized from natural sources like *Acacia arabica* plant. A series of carbon-doped MoO_3 nanocomposite materials were prepared by sol-gel method. As a part of our research interest towards the development of efficient, environmentally benign and green synthetic methodologies using eco-friendly conditions, the motivation for this work was the investigation of novel synthetic route to prepare realistic solid acid catalytic model system based on molybdenum oxide by using PEG-400 and natural carbon, which should give an efficient and environmentally friendly process for the synthesis of 3,4-dihydropyrimidones via the Biginelli-type condensation reaction. The prepared catalyst is inexpensive, solid, non-corrosive and recyclable. The short reaction time, clean reaction condition, consistent yield and minimum environmental effect are important features of the reaction.

Experimental

X-ray diffraction analyses (XRD) of the Molybdenum oxide and carbon-doped MoO_3 with and without PEG-400 particles were performed using a Philips X-ray diffractometer. The wavelength used for the XRD analysis was 1.54 Å with radiation of CuKα. The diffracting angle was varied between 20°—80°. Surface morphology and elemental analysis of the samples were carried out using Scanning Electron Microscopy with Electron Dispersion Spectroscopy (SEM-EDS) characterization conducted using a JEOL JEM 2300 (LA) instrument. The Fourier Transformation Infra-Red spectra (FT-IR) were recorded on FT-IR spectrometer (JASCO FTIR/4100, Japan) in the range of 4000—500 cm^{-1}. The microscopic nanostructures and particle size were determined using a CM-200 PHILIPS Transmission Electron Microscope (TEM) at 200 kV ($L=600$, $\lambda=0.025$ Å).

The reagent grade chemicals were used in the preparation of the samples, ammonium heptamolybdate (Ranbaxy Fine Chemicals), oxalic acid (Ranbaxy Fine Chemicals), ammonia (Ranbaxy Fine Chemicals), poly(ethylene glycol)-400 (PEG-400) (Qualigens Fine Chemicals), without further purification.

Preparation of carbon substrate

The carbon was prepared from *Acacia arabica* plant as a natural source. In the first step dried wood was burnt in absence of air, then resulting charcoal was crushed into fine powder. Finally, the obtained powder material was calcined at 500 ℃ in high temperature muffle furnace in air atmosphere. The temperature stability of carbon is estimated to be up to 2800 ℃ in vacuum and about 750 ℃ in air.[26]

Preparation of carbon-doped MoO_3

Carbon-doped MoO_3 catalysts were prepared by conventional standard impregnation method. To impregnate carbon-doped MoO_3, the solution was obtained by dissolving ammonium heptamolybdate (0.2 mol/L) in deionized water. The system was kept under constant stirring and sustaining the pH=8 by simultaneous addition of 1∶1 NH_4OH.[27] The fine powdered carbon was added with 0 wt% (CM-0), 1 wt% (CM-1), 2 wt% (CM-2) and 3 wt% (CM-3), respectively. The excess water was evaporated on the water bath with continuous stirring. The resultant precursor was then dried at 110 ℃ for 12 h and calcined at 500 ℃ for 2 h in air atmosphere.

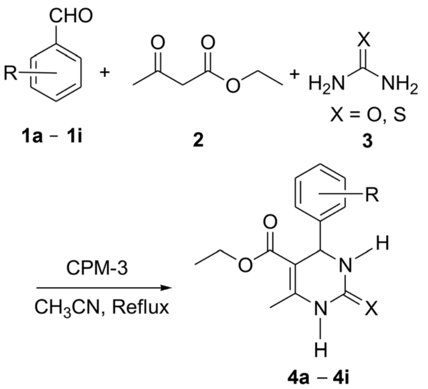
Preparation of carbon-doped MoO_3 with PEG-400

The series of modified samples with the addition of carbon powder to solution containing PEG-400 on MoO_3 were prepared by simple impregnation method, such as CPM-0, CPM-1, CPM-2, CPM-3 respectively.[28] The fine powdered carbon (0, 1, 2, 3 wt%) was added in the solution. Then excess water was evaporated with continuous stirring. It was then dried at 110 ℃ for 12 h and calcined at 500 ℃ for 2 h in air atmosphere.

General procedure for the synthesis of substituted 3,4-dihydropyrimidinones

As shown in Scheme 1, a mixture of aldehydes (1 mmol), ethyl acetoacetate (1 mmol) and urea/thiourea (1.5 mmol) in the presence of carbon-doped MoO_3 with and without PEG-400 (0.2 mmol) in acetonitrile as solvent was refluxed at 70—80 ℃ for an appropriate time to gave 3,4-dihydropyrimidinone. After completion of the reaction monitored by TLC (hexane/ethyl acetate, 8∶2), the reaction mixture was brought to room temperature. Reaction mixture was washed by cold water to remove excess urea or thiourea and then filtered. The remaining solid material was washed with hot ethyl acetate. The filtrate was concentrated and the solid product was recrystallized from ethanol to give the pure product. Many substitution patterns on the aromatic ring could be introduced with high efficiency. We noted that all aromatic aldehydes carrying either electron-donating or electron-withdrawing substituents reacted well; giving moderate to excellent yields. The structure of all the products was confirmed by comparing melting point and spectral data with those in the literature.

Scheme 1 Preparation of substituted 3,4-dihydropyrimidinones from benzaldehyde, ethylacetoacetate and urea or thiourea by using CPM-3 catalyst in acetonitrile solvent with reflux



Physical and spectroscopic data

3,4-Dihydro-6-methyl-4-phenyl-5-propionylpyrimidin-2(1*H*)-one (**4a**): ^{1}HNMR ($CDCl_3$, 300 MHz) δ: 8.40 (s, 1H), 8.07(s, 1H), 7.26—7.38 (m, 5H), 5.45 (d, $J=2.15$ Hz, 1H), 4.08 (q, $J=6.90$ Hz, 2H), 2.36 (s, 3H), 1.19 (t, $J=7.10$ Hz, 3H); IR (KBr) ν: 3240, 1722, 1638 cm^{-1}.

3,4-Dihydro-6-methyl-5-propionyl-4-*p*-tolylpyrimidin-2(1*H*)-one (**4b**): ^{1}HNMR ($CDCl_3$, 300 MHz) δ: 8.10 (s, 1H), 7.94 (s, 1H), 7.26—7.38 (m, 5H), 5.35 (d, $J=2.05$ Hz, 1H), 4.11 (q, $J=6.09$ Hz, 2H), 2.35 (s, 3H), 1.71 (s, 3H), 1.19 (t, $J=7.80$ Hz, 3H); IR (KBr) ν: 3240, 1722, 1638 cm^{-1}.

4-(4-Chlorophenyl)-3,4-dihydro-6-methyl-5-propionylpyrimidin-2(1*H*)-one (**4c**): ^{1}HNMR ($CDCl_3$, 300 MHz) δ: 8.08 (s, 1H), 7.85 (s, 1H), 7.58 (d, $J=9.90$ Hz, 2H), 7.32 (d, $J=9.08$ Hz, 2H), 4.38 (d, $J=6.80$ Hz, 1H), 4.12 (q, $J=7.20$ Hz, 2H), 2.37 (s, 3H), 1.28 (t, $J=7.15$ Hz, 3H); IR (KBr) ν: 3225, 1720, 1615 cm^{-1}.

3,4-Dihydro-6-methyl-4-(3-nitrophenyl)-5-propionylpyrimidin-2(1*H*)-one (**4d**): ^{1}HNMR ($CDCl_3$, 300 MHz) δ: 8.38 (s, 1H), 8.15 (s, 1H), 7.75 (d, $J=9.18$ Hz, 2H), 7.48 (d, $J=9.18$ Hz, 2H), 5.05 (d, $J=2.25$ Hz, 1H), 3.97 (q, $J=7.20$ Hz, 2H), 2.42 (s, 3H), 1.30 (t, $J=7.24$ Hz, 3H); IR (KBr) ν: 3232, 1724, 1631 cm^{-1}.

4-(4-Fluorophenyl)-3,4-dihydro-6-methyl-5-propionylpyrimidin-2(1*H*)-one (**4e**): ^{1}HNMR ($CDCl_3$, 300 MHz) δ: 8.08 (s, 1H), 7.85 (s, 1H), 7.65 (d, $J=9.08$ Hz, 2H), 7.28 (d, $J=8.95$ Hz, 2H), 5.45 (d, $J=2.20$ Hz, 1H), 4.11 (q, $J=7.17$ Hz, 2H), 2.37 (s, 3H), 1.28 (t, $J=7.16$ Hz, 3H); IR (KBr) ν: 3232, 1724, 1631 cm^{-1}.

4-(2-Chlorophenyl)-3,4-dihydro-6-methyl-5-propionylpyrimidin-2(1*H*)-one (**4f**): ^{1}HNMR ($CDCl_3$, 300 MHz) δ: 8.38 (s, 1H), 8.11 (s, 1H), 7.35 (d, $J=9.10$ Hz, 2H), 7.08 (d, $J=9.08$ Hz, 2H), 5.45 (d, $J=2.18$ Hz, 1H), 4.08 (q, $J=7.10$ Hz, 2H), 2.36 (s, 3H), 1.19 (t, $J=7.44$ Hz, 3H); IR (KBr) ν: 3250, 1741, 1654 cm^{-1}.

1-(1,2,3,4-Tetrahydro-6-methyl-2-thioxo-4-*p*-tolylpyrimidin-5-yl)propan-1-one (**4g**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.05 (s, 1H), 7.75 (s, 1H), 7.26—7.40 (m, 4H), 5.35 (d, $J=3.05$ Hz, 1H), 4.21 (q, $J=6.90$ Hz, 2H), 2.45 (s, 3H), 1.31 (s, 3H), 0.90 (t, $J=7.80$ Hz, 3H); IR (KBr) ν: 3240, 1722, 1638 cm^{-1}.

1-(4-(4-Chlorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidin-5-yl)propan-1-one (**4h**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.75 (s, 1H), 8.51 (s, 1H), 8.25 (d, $J=7.88$ Hz, 2H), 7.88 (d, $J=7.58$ Hz, 2H), 5.45 (d, $J=2.05$ Hz, 1H), 4.32 (q, $J=7.15$ Hz, 2H), 1.71 (s, 3H), 1.32 (t, $J=7.01$ Hz, 3H); IR (KBr) ν: 3245, 1725, 1632, 1575, 1545 cm^{-1}.

1-(1,2,3,4-Tetrahydro-6-methyl-4-(3-nitrophenyl)-2-thioxopyrimidin-5-yl)propan-1-one **(4i)**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.15 (s, 1H), 8.08 (s, 1H), 7.25 (d, $J=9.35$ Hz, 2H), 7.18 (d, $J=9.00$ Hz, 2H), 5.45 (d, $J=2.05$ Hz, 1H), 4.17 (q, $J=7.51$ Hz, 2H), 1.88 (s, 3H), 1.19 (t, $J=7.10$ Hz, 3H); IR (KBr) ν: 3250, 1741, 1654.

Results and discussion

XRD analysis

In order to understand the phase symmetry of the calcined samples, a systematic study on the XRD was undertaken. Figure 1 shows that the highly intense peaks were obtained at $2\theta=22.98°$, 25.36°, 29.33°, 35.94°, 39.40°, 43.19° and 47.35°, corresponding to planes (320), (400), (421), (440), (532), (542) and (552), respectively, which predicts the cubic crystal symmetry

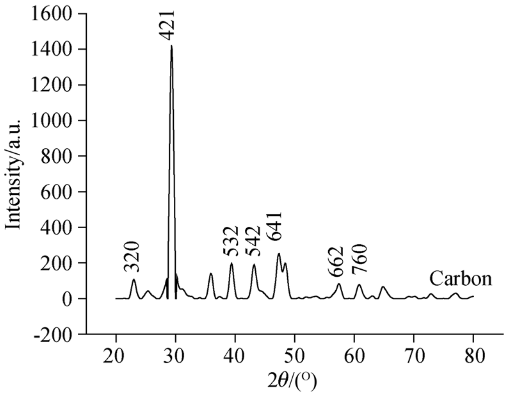


Figure 1 XRD patterns of carbon sample prepared from *Acacia arabica*.

of carbon substrate or fullerene. It was found that all the XRD reflections of carbon substrate were matched using JCPDS card No. 79-7015[29] and lattice parameter ($a = b = c = 14.0408$ Å).

Figure 2 (a—d) shows the XRD patterns of carbon doped MoO_3 without PEG-400 addition, *i,e*, CM-0, CM-1, CM-2 and CM-3 samples which gives highly intense and sharp peaks at $2\theta = 23.36°$, 25.75°, 27.30°, 33.61° and 38.96°, corresponding to the planes (110), (040), (021), (111) and (060), respectively, indicating orthorhombic crystal structure. The average particle sizes of the powder were calculated using Debye-Scherrer formula.[30] It was noted that all the XRD peaks are identified as MoO_3 peaks from the JCPDS card 76-1003,[31] with lattice parameter $a = 3.9628$ Å, $b = 13.8550$ Å and $c = 3.6964$ Å. The strong and sharp peaks suggest that the as-prepared materials are crystalline. Additional peak observed in Figure 2d at $2\theta = 30.00°$ for the plane corresponds to 421.

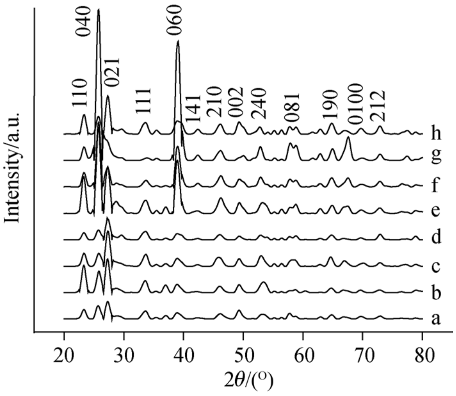


Figure 2 The XRD patterns of carbon doped MoO_3 with and without PEG-400 addition. (a) CM-0, (b) CM-1, (c) CM-2, (d) CM-3, (e) CPM-0, (f) CPM-1, (g) CPM-2, (h) CPM-3.

The Figure 2 (e—h) shows the XRD patterns of carbon doped MoO_3 with PEG-400 addition, *i.e.* CPM-0, CPM-1, CPM-2 and CPM-3, which identifies the planes (110), (040), (021), (111) and (060), corresponding to orthorhombic crystal symmetry. Due to addition of PEG-400, it was interestingly noted that the high intensity peak was observed at 38.95° (2θ for *hkl* 060). The XRD analysis comparison data of pure MoO_3 and 3% carbon doped MoO_3 with PEG-400 were summarized in Table 1. It was observed that all the XRD peaks are exactly matched with literature values for MoO_3 peaks. A single orthorhombic structure was found for the entire range of concentration of carbon.[32,33] Similar peak observed in Figure 2h at 2θ 30.00° for the plane corresponds to 421.

SEM and EDS analysis

To study the surface topography and elemental composition, the SEM and EDS were investigated systematically. Figure 3a shows flakes structure of carbon. Figure 2 (b—g) shows the variation in morphology of MoO_3 samples with and without PEG-400 and carbon addition. Figure 3 (b—c) shows morphology of pure CM-0 with crystalline nature. It can be seen that the samples CM-3 show agglomeration and randomness in the particle size without porosity in Figure 3 (d—e). Further, the samples CPM-3 show decrease in the particle size and development of porous surface in Figure 3 (f—g). From the SEM micrograph it can be seen that effect of addition of PEG-400 as a surfactant clearly shows alteration in particle size and morphology with increasing porosity.

Table 1 XRD analysis comparison data of CM-0 and CPM-3

h k l	2θ/(°) (Calc.)	2θ/(°) (Exp.)	CM-0 *d*/Å	CPM-3 *d*/Å	Grain size/nm
1 1 0	23.334	23.313	3.80483	3.81257	10.16
0 4 0	25.078	25.692	—	3.46471	09.11
0 2 1	27.330	27.294	3.2663	3.26487	09.76
1 1 1	33.763	33.615	2.66388	2.66391	07.64
0 6 0	38.987	38.933	2.30947	2.31146	06.40
1 4 1	42.393	42.312	2.13012	2.13435	06.29
2 1 0	46.258	46.157	1.96485	1.96510	06.13
0 0 2	49.269	49.292	1.84684	1.84719	08.54
2 4 0	53.229	53.218	—	1.71981	05.50
1 7 1	57.698	57.759	1.59417	1.59491	08.98
2 5 1	62.867	62.939	1.47614	1.47555	10.08
1 9 0	64.958	64.806	1.43729	1.43748	08.03
2 7 0	66.768	66.821	—	1.39893	05.38
0 7 2	69.551	69.699	1.34777	1.34803	06.82
2 3 2	72.877	72.922	1.29654	1.29620	07.21
3 0 1	76.542	76.511	—	1.24409	07.57
0 2 3	78.878	78.878	—	1.21258	08.58

Elemental compositions of carbon doped MoO_3 with and without PEG-400 were presented in Table 2. The observed Mo∶C∶O atomic ratios are fairly close to the expected bulk ratios indicating also a rather good distribution of the metal species inside the samples. It showed that, the minimum stoichiometric ratio of desired elements in the CM_3 and CPM_3 maintained.

FT-IR analysis

Figure 4a shows the FT-IR spectra of the carbon substrate. The spectrum of the carbon substrate shows broad peaks at 3400 cm^{-1} due to OH stretching vibration modes of the absorbed water, the peak at 1384 and 1576 cm^{-1} could be assigned for C—C and C=C vibration respectively.[34] Figure 4b shows the FT-IR spectra of CM-0 (pure MoO_3). A band at 878 cm^{-1} is characteristics of terminal molybdenum oxygen double bond (Mo=O). The bands at 1439 and 1577 cm^{-1} were attributed to C—C and C=C vibrations. The broad band around 3499 cm^{-1} was due to O—H stretching vibration modes of the adsorbed water on the surface of the powder.[35]

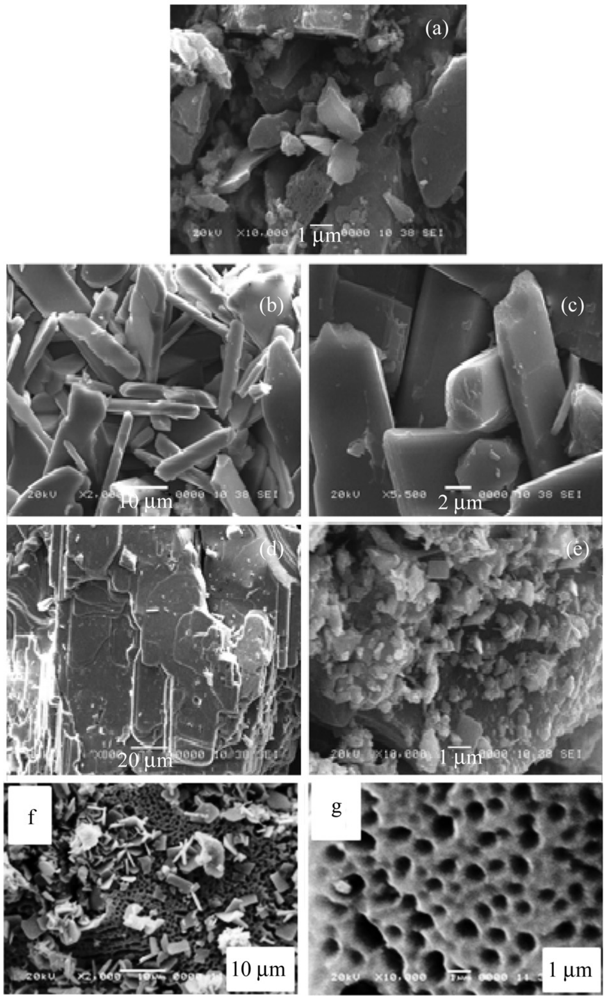


Figure 3 The SEM image of (a) carbon, (b) and (c) CM-0, (d) and (e) CM-3, (f) and (g) CPM-3.

Table 2 EDS elemental quantitative analysis

Entry	Sample	Elemental atomic wt%		
		Mo	O	C
1	CM-3	13.12	44.09	42.79
2	CPM-3	9.58	34.51	55.91

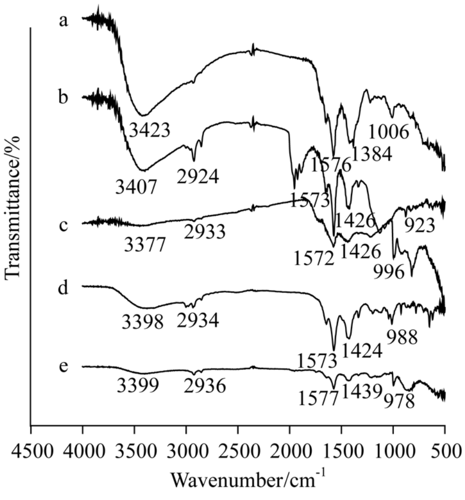


Figure 4 IR spectra of (a) carbon, (b) CM-0, (c) CM-1, (d) CM-2, (e) CM-3.

Figure 4 (c—e) shows the FT-IR spectra of CM-1, CM-2 and CM-3 respectively. A sharp band appearing in the range 875—885 cm^{-1} is due to the terminal molybdenum-oxygen double bond (Mo=O). The bands at 1410—1600 cm^{-1} were attributed to C—C and C=C vibrations, the additional band around 2926 cm^{-1} probably may be due to CH_2 and or C(OH) stretching mode. While broad band around 3381—3464 cm^{-1} was due to O—H stretching vibration modes of the adsorbed water.[36] Figure 5 (a—d) shows the FT-IR spectra of CPM-0, CPM-1, CPM-2 and CPM-3. The bands observed were similar to the samples without addition of PEG-400. We cannot find any bands for PEG-400, because the flash point of PEG is in between 182—287 ℃.

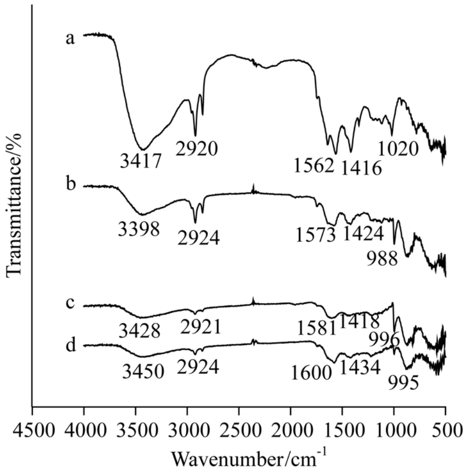


Figure 5 IR spectra of (a) CPM-0, (b) CPM-1, (c) CPM-2, (d) CPM-3.

TEM analysis

The TEM images shown in Figure 6 indicate the obtained nano-sized particles for clarity. The TEM image of pure MoO_3 in Figure 6a shows the presence of highly crystalline nano rods of MoO_3 with particles size varing in between 15.34 to 20.70 nm. It can be also seen that in Figure 6 (c, d) the average particle size of modified sample of carbon doped MoO_3 with PEG-400 addition (CPM-3) is in the range of 10.42 to 18.57 nm. From the electron diffraction patterns (EDP) shown in Figure 6b, R was measured to obtain the d value using the following equation with known values of λ and L.

$$\lambda L = Rd$$

where, R is the distance of a diffraction spot from the direct beam spot on the diffraction pattern, d is the spacing of the planes; L is the effective camera length and λ is wavelength of radiation. The value of λL is referred to as the camera constant of the microscope. The obtained d values of 3.86, 3.50, and 3.04 indicated the (320), (400), and (421) surfaces of the orthorhombic form of MoO_3.

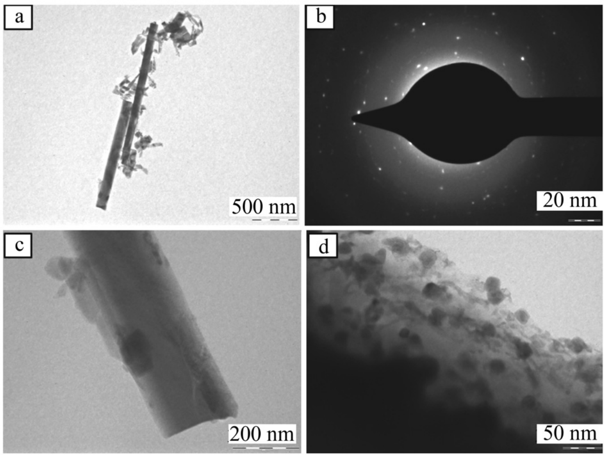


Figure 6 TEM images of (a) pure MoO_3, (b) pure TiO_2, (c) MoO_3 doped TiO_2 and (d) high magnification of MoO_3 doped TiO_2.

Catalytic activity results

In order to get best experimental results, we have considered the model reaction of Biginelli's one-pot condensation reaction, *i.e.* that the reaction of aldehydes (1.0 mmol) with urea or thiourea (1.2 mmol) and ethyl acetoacetate (1.2 mmol) using 0.1 g of catalyst in acetonitrile (10 mL) as solvent at ambient temperature. The reaction is very fast and 93% conversion was observed in 90—180 min. In this study, the effect of different solvent was investigated and the results are given in Table 3. The choice of solvent proved critical. The results showed that the examined solvents were not suitable separately. The best result was found to be with 0.1 g of CPM-3 catalyst, affording 93% yield of product. It was observed that the acetonitrile is a much better solvent in terms of yields (93%) than all other tested solvents such as methanol, dichloromethane, THF, water, H_2O-THF and toluene.[37]

Table 3 Comparative study of different solvent system

Entry	Solvent	Time/min	Yield/%
1	EtOH	180	35
2	Acetic acid	180	40
3	CH_3CN	90	93
4	CH_3OH	120	82
5	CH_2Cl_2	120	76
6	THF	180	65
7	H_2O	180	40
8	H_2O-THF	180	70
9	Toluene	180	60

Reaction condition: benzaldehyde (1.0 mmol) with ethyl acetoacetate (1.2 mmol) and urea (1.2 mmol) using 0.1 g of CPM-3 catalyst in 10 mL solvent in refluxing.

We initially studied the effect of prepared catalysts for the Biginelli's one-pot condensation reaction. As shown in Table 4, the choice of catalyst significantly affected the product yield. Among these catalysts, CPM-3 was proved to be the best as compared to the others (Table 4, Entry 8). The CPM-3, the catalytic material exhibits very good catalytic activity in the synthesis of substituted 3,4-dihydropyrimidinones with excellent to high yield in very shorter reaction time. That might be due to small particle size and high porosity. The possible mechanism for the preparation of substituted 3,4-dihydropyrimidinones by using CPM-3 catalyst is presented in Scheme 2. In order to strengthen the novelty of present method, we have compared our results with some reported procedures using some other catalysts such as $Cu(NH_2SO_3)_2$, $Bi(NO_3)_3$, $Pb(NO_3)_2$, aq. $Zn(BF_4)_2$, H_2SO_4/SiO_2.[38-42] It was observed that CPM-3 catalytic materials give high yields within very short reaction times in comparison with earlier reported methods.

Table 4 Effect of carbon and PEG-400 content of the catalyst

Entry	Catalyst	Time/min	Yield/%
1	CM-0	180	51
2	CM-1	120	62
3	CM-2	120	65
4	CM-3	90	76
5	CPM-0	120	55
6	CPM-1	120	70
7	CPM-2	90	82
8	CPM-3	90	93, 91, 91[a]

Reaction condition: benzaldehyde (1.0 mmol) with ethyl acetoacetate (1.2 mmol) and urea (1.2 mmol) using 0.1 g of catalyst in 10 mL acetonitrile solvent in refluxing. [a] Yield of product with catalyst reused up to three times.

Therefore, the CPM-3 catalytic material in acetonitrile solvent system in refluxing was used for the preparation of different derivatives of 3,4-dihydropyrimidinones with electron donating as well as withdrawing substituent. Similarly, we study the tolerance of various functional groups such as methyl, chlorides, nitro and fluorides, *etc*. to the reaction conditions. Aromatic aldehyde with these functional groups reacted smoothly and produced the corresponding dihydropyrimidinones in high yields and high purity. Thiourea has been used with similar success to provide corresponding *S*-dihydropyrimidinones analogues, which are also of interest due to their biological activities (Table 5). The catalyst was recovered by filtration of reaction mixture under hot condition. The recovered catalyst was washed several times with acetone and dried at 100 ℃. The separated catalyst was again reused for the same reaction. In these cases the yield of product to be 93%, 91%, 91% in successive three-time use. Thus the activity of catalyst was found to be diminished after its recyclability.

The reaction proceeds efficiently under these conditions and the dihydropyrimidinones are produced in

Scheme 2 Possible mechanism for the preparation of substituted 3,4-dihydropyrimidinones by using CPM-3 catalyst

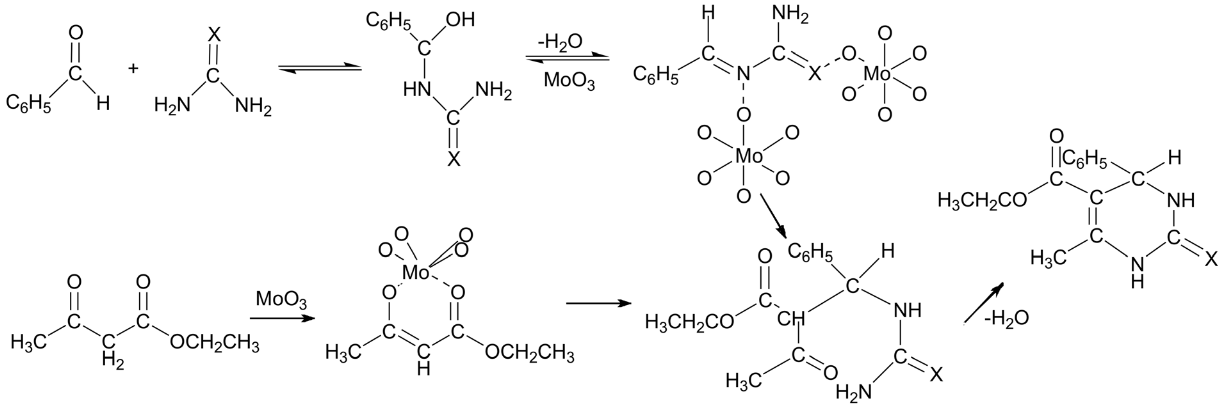


Table 5 Preparation of different derivatives of 3,4-dihydropyrimidinones

Entry	R	X	Time/min	Yield/%	m.p. (Rep.)/℃	m.p. (Found)/℃
a	H	O	85	93	200—202	206—208
b	4-CH_3	O	135	88	214—216	212—214
c	4-Cl	O	120	90	212—213	215—216
d	3-NO_2	O	150	90	225—226	227—229
e	2-Cl	O	140	81	219—222	215—218
f	4 -F	O	125	89	175—177	178—180
g	4-CH_3	S	160	87	193—195	192—194
h	3-NO_2	S	140	91	204—205	205—207
i	4-F	S	145	90	—	236—238

Reaction condition: benzaldehyde (1.0 mmol) with ethyl acetoacetate (1.2 mmol) and urea (1.2 mmol) using 0.1 g of CPM-3 in 10 mL acetonitrile solvent in refluxing to 90 min.

excellent yields (93%) in short reaction times (90 min). This procedure using carbon-doped MoO_3 with PEG-400 as a catalyst for the synthesis of dihydropyrimidinones offers several advantages including mild reaction conditions, greater selectivity, high product yields as well as simple experimental and isolation procedure, which makes it a useful and attractive process for large scale synthesis of these compounds.

Conclusions

In summary, an efficient catalytic system has been developed for the synthesis of 3,4-dihydropyrimidones derivatives via Biginelli-type reaction. Present method offers remarkable advantages such as non-toxic, non-corrosive and an inexpensive reaction condition. Simply recovery and reusability of the catalyst makes the reaction successful under environmental benign conditions.

Acknowledgements

The authors are grateful to the Head, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for providing the all required facilities to carry out the work.

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(E1105063 Sun, H.)