ZnO nanoparticles embedded in SBA-15 as an efficient heterogeneous catalyst for the synthesis of dihydropyrimidinones via Biginelli condensation reaction

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Abstract
A new ZnO@SBA-15 nanocomposite material has been fabricated by an “in situ” generation of ZnO NPs on SBA-15 support. The as-synthesized nanocomposite material was fully characterized with various spectroscopic techniques and their catalytic activity was tested for the synthesis of a diverse range of dihydropyrimidinones (DHPMs) and thione derivatives via Biginelli condensation reaction. The catalytic efficiency of ZnO@SBA-15 nanocomposite was far superior with a remarkably lower catalyst loading and shorter reaction time compared to unsupported ZnO nanoparticles. The catalyst was recycled for minimum of four times without significant loss in its catalytic activity. Moreover, a tentative catalytic cycle for the reaction is also proposed.

1. Introduction

Multicomponent reactions (MCRs) have become current research interest to the synthetic organic chemist owing to their synthetic efficiency, atom economy and procedural simplicity. The combinatorial chemistry of these reactions allows synthesizing large library of structurally related compounds. MCRs are also an important tool to the modern drug development research so as to achieve a synthetic target in an expeditious way. Furthermore, MCRs are environmentally benign processes and their one pot synthesis chemistry reduces the energy consumption and byproduct formation [1]. Biginelli reaction is one of the most studied multicomponent reaction that used to synthesize dihydropyrimidinones (DHPMs), an important class of compounds that have diverse pharmacological properties [2]. This reaction attracted much attention after the discovery of calcium channel modulator drug nifedipine which features DHPM backbone, used in the treatment of cardiovascular diseases [3]. Monastrol, an anticancer agent that can specifically inhibit mitotic kinesin Eg5 [4]. DHPMs compounds viz SQ 32547 and SWO2, are effective orally active antihypertensive agents [5]. Most notably, several alkaloids extracted from marine sources having DHPM as their core building blocks shows interesting biological properties. Batzelladine is one of such marine natural alkaloid have shown its activity as potent HIV gp-120-CD4 inhibitors [6]. Some ester, cyanide substituted DHPMs are reported to be promising antibacterial agents [7]. Several pyrimidinone-amide derivatives of DHPMs are tested as anti-malarial agents, a new class of Hsp70 modulators, could inhibit the replication of the pathogenic P. falciparum stages in human red blood cells [8]. A series of compounds 3-(4,6-disubstituted-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl) propanoic acid derivatives showed significant anti-inflammatory activity [9]. The classical Biginelli reaction involves one pot condensation of an aldehyde, a β-ketoester (active methelene compound) and urea or thiourea under strongly acidic conditions [10]. The main drawbacks of this classical method is the harsh reaction conditions, longer reaction times, and lower yields when substituted aromatic and aliphatic aldehydes are used as substrates [11]. So the classical Biginelli reaction is not suitable for substrates having acid-sensitive functional groups. In order to increase the product yield, various homogeneous [12] and heterogeneous [13] catalysts are used for the Biginelli reaction but both homogenous and heterogeneous catalysts have severe limitations. The high temperature, longer reaction...
time, high catalyst loading needed for homogenous catalysts whereas heterogeneous catalysts also had metal leaching problem apart from the same limitation as homogeneous catalysts.

Metal oxide is widely used as catalyst in many important organic transformations. The main features of the metal oxide is their stability, recyclability, non-toxic, non-hygroscopic properties which make it an efficient catalyst [14–16]. Zinc Oxide (ZnO) is one of such metal oxide and it has previously demonstrated its catalytic activity for many organic transformations [15,16]. But unsupported ZnO NPs has one major drawback that it generally aggregated during the synthesis process which reduces its surface area and thereby reducing active catalytic sites for adsorption of reagents [16,17]. Due to this reasons, high catalyst loading and longer reaction time required for many ZnO catalysed reactions [17]. But this problem can be solve by increasing the dispersion of ZnO nanoparticles (NPs) on a high surface area support such as mesoporous SBA-15. SBA-15 is one of the most well studied mesoporous silica-based material having very high specific surface area, highly uniform 2D hexagonal array of pores, good thermal and hydrothermal stability [18]. It serves as a support for various metal and metal oxide NPs that are investigated for catalytic application [19,20]. Recently D. Bhuyan et al. demonstrated that catalytic activity of unsupported magnetic Fe2O3 NPs can be enhanced by supporting it on mesoporous SBA-15 for the A [3] coupling reaction [20c]. Moreover, PEG-4000 used in our synthesis method provided better distribution of uniform sized ZnO NPs over existing methods which often result aggregated ZnO NPs [21,26].

In the present work, we have synthesized ZnO NPs on SBA-15 support by a calcination process. The as-synthesized ZnO NPs have very narrow size distribution, well dispersed and very high surface area. Furthermore the as-synthesized ZnO NPs exhibited enhanced catalytic activity for Biginelli condensation reaction and a diverse range of DHPMs compounds were synthesized.

2. Experimental section

2.1. Chemicals

Tetaethyl orthosilicate (TEOS), Pluronic P123 triblock copolymer (EO{sub d}PO{sub 70}EO{sub b}, average molecular weight = 5800) were procured from Sigma-Aldrich. HCl (Merck), Zinc acetate dihydrate (Alfa Aesar), ZnO nanopowder (<50 nm average particle size, Sigma-Aldrich) and Polyethylene glycol-4000 (SRL) were procured from the mentioned chemical companies. All chemicals are analytical grade and used as received without further purification.

2.2. Characterization

Low angle X-ray diffraction patterns were recorded on a Philips X’Pert Pro diffractometer in the 20 range from 0.5 to 5° using Cu Kα radiation. Wide angle X-ray diffraction measurement were performed on a Rigaku, Ultima IV X-ray diffractometer in the 20 range of 10–90° using Cu Kα source (λ = 1.54 Å). The N2 adsorption-desorption isotherm measurement was carried out on Autosorb-1 (Quantachrome, USA). Prior to analysis, the samples were degassed at 250°C for 3 h under high vacuum conditions. Brunauer–Emmett–Teller (BET) calculation was used to determine the specific surface areas of the samples. Pore size distributions were derived from desorption isotherms using the Barret–Joyner–Halenda (BJH) method. The Transmission electron microscopy (TEM) images of the samples were recorded on a JEOL JEM-2011 transmission electron microscope operated at 200 KV. Field emission scanning electron microscopy (FESEM) images were obtained from a Carl Zeiss Sigma FESEM instrument. Energy dispersive X-ray spectroscopy (EDS) pattern and elemental mapping analysis was recorded on Oxford X Max 20 equipment. FT-IR spectra (4000–400 cm−1) were recorded as KBr pellets in a Shimadzu IR affinity-1 spectrophotometer. The absorbance spectra was recorded at room temperature using a UV-visible spectrophotometer (Model Shimadzu 1601 pc) as aqueous dispersion. The Atomic absorption spectroscopy (AAS) measurement was carried out using PerkinElmer (Model AAnalyast-700) spectrometer. Prior to AAS analysis, the sample was digested in aqua regia.1H and 13C NMR data of the products were recorded at room temperature in a Bruker DPX-300 NMR spectrometer using DMSO-d6 as the solvent. Melting point data of the samples were obtained from a Büchi melting point apparatus (Model M560).

2.3. Synthesis of SBA-15 material

SBA-15 was synthesized according to the reported literature by D. Zhao et al. using tetraethyl orthosilicate (TEOS) as the silica source, Pluronic P123 triblock copolymer as the template and HCl as the pH controlling agent [18a,20c].

2.4. Synthesis of ZnO NPs supported on mesoporous SBA-15

Zinc acetate dihydrate (0.1 g) and PEG-4000 (0.1 g) were dissolved in 50 mL double distilled water by vigorous stirring. After that, NH3 solution was added to the mixture until the pH of the solution became 9.7. Then the resulting solution was heated at 80°C for 8 h and cool down naturally. Thereafter calcined SBA-15 (1 g) was added to the solution and sonicated for 30 min. The precipitate then filtered off and dried in vacuum desiccator. Finally, the precipitate was calcined at 450°C for 12 h at the heating rate of 3°C/min and cool to room temperature naturally. The as-synthesized material is designated as ZnO@SBA-15 nanocomposite.

General procedure for the synthesis of DHPMs by Biginelli condensation reaction.

A mixture of the aldehyde (1 mmol), ethyl or methyl-acetoacetate (1 mmol), urea or thiourea (1.4 mmol), ethanol (2 mL) and 20 mg ZnO/SBA-15 catalyst (3.12 wt% ZnO) was stirred in a glass tube at 65°C. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by filtration and the solvent was evaporated under reduced pressure to obtain a solid product. Then ethyl acetate (20 mL) was added to the solid product. The resulting organic layer was washed with 10% NaHCO3 and brine solution, dried over anhydrous Na2SO4 and evaporated to give the desired product. The solid product was further purified by re-crystallization from ethanol. The re-crystallized pure products was characterized by 1H NMR, 13C NMR, melting point measurement respectively and compared with the reported data.

3. Result and discussion

Fig. 1(a) shows the low angle XRD patterns of as-synthesized SBA-15 materials which displayed three well resolved peaks indexed to the (100), (110) and (200) planes. These planes correspond to the 2D hexagonal symmetry and long range mesoporous ordering, characteristic for SBA-15 [18]. The retention of aforementioned peaks in case of ZnO@SBA-15 nanocomposite confirmed that calcination process did not change mesopores ordering of SBA-15 support [21]. However, the observed shift in 20 values as well as decrease in intensity of the planes for ZnO@SBA-15 is due to the presence of ZnO NPs which may partly block the pores so as to decrease the mesopores ordering a little [22]. Wide angle XRD patterns [Fig. 1 (b)] shows a broad band in between 20 angle value of 15 and 35° which is the characteristic band of amorphous SBA-15 [23]. For ZnO@SBA-15 nanocomposite, in addition to the broad
characteristic band of SBA-15, nine extra diffraction peaks were observed at $2\theta = 32.1^\circ$, 34.6$^\circ$, 36.5$^\circ$, 47.9$^\circ$, 56.9$^\circ$, 63.2$^\circ$, 66.5$^\circ$, 68.2$^\circ$ and 69.3$^\circ$ that corresponds to the (100), (002), (101), (102), (110), (103), (200), (122) and (201) reflections respectively. These diffraction peaks clearly corresponds to the hexagonal wurtzite structure of pure ZnO (JCPDS 36–1451) without traces of any other impurity [21,24]. The crystallite size of the ZnO NPs was found to be 16 nm which has been calculated from the Scherrer equation, using PDXL software. The recovered ZnO@SBA-15 nanocomposite catalyst after 5th run retained all characteristic peaks of ZnO NPs and SBA-15 (Fig. S1, ESI).

The surface and structure properties of SBA-15 and ZnO@SBA-15 were evaluated using N$_2$ adsorption-desorption isotherm analysis. Fig. 2 shows the N$_2$ adsorption-desorption isotherm and pore distribution curve [Fig. 2 inset] of SBA-15 and ZnO@SBA-15 respectively. SBA-15 shows their characteristics type IV isotherm with a H1 hysteresis loop and BJH pore distribution curve which confirm its monodispersed ordered mesoporousity [21]. The sharp inflexion observed in the relative pressure ($P/P_0 = 0.6–0.8$) corresponds to the capillary condensation [25]. The BET surface area, total pore volume, average pore diameter of SBA-15 was found to be 559 m$^2$/g, 1.03 cm$^3$/g and 7.4 nm respectively. For ZnO@SBA-15, type IV isotherm with a H1 hysteresis loop was also observed which means that generation of ZnO NPs on SBA-15 did not change its mesoscopic ordering [21]. But shifting as well as decrease in sharpness of the inflexion in the relative pressure ($P/P_0 = 0.65–0.8$) of capillary condensation was observed due to pore blocking effect [23]. The same reason is responsible for decrease in BET surface area (341 m$^2$/g) and total pore volumes (0.75 cm$^3$/g). However because of calcination process average pore diameter (7.9 nm) of ZnO@SBA-15 nanocomposite was increased a little than the SBA-15.

The transmission electron microscopy (TEM) image of SBA-15 clearly shows the well-defined monodispersed ordered honeycomb like 2D hexagonal array of mesopores [Fig. 3 (a)] [21]. The long range mesoporous ordering of SBA-15 is retained even after the generation of ZnO NPs [Fig. 3 (b), (c) and (d)]. The black dots

**Fig. 1.** (a) Low angle and (b) Wide angle XRD patterns of as-synthesized SBA-15 materials.

**Fig. 2.** N$_2$ adsorption–desorption isotherms and BJH pore size distribution curves (inset), (a) SBA-15 and (b) ZnO@SBA-15 nanocomposite material.
observed in these TEM images is the ZnO NPs, expected to present in both inside mesoporous channel and the surface of SBA-15 [26]. The ZnO NPs supported on SBA-15 has an average size of 3.8 nm which was calculated from the particle size distribution curve [Fig. 3 (e)]. Moreover the selected area electron diffraction (SAED) pattern confirmed the single crystalline nature of ZnO NPs [Fig. 3 (f)]. The TEM images of the recovered ZnO@SBA-15 nanocomposite catalyst after 5th run (Fig. S2, ESI) shows no deterioration in the mesoscopic ordering of SBA-15.

The Zn contents of the ZnO@SBA-15 nanocomposite was found to be 2.51 wt% from the atomic absorption spectroscopy (AAS) analysis. As only ZnO is present in the sample so the amount of ZnO can be calculated from Zn content which is 3.12 wt%.

The field emission scanning electron microscopy (FESEM) images, energy dispersive X-ray spectroscopy (EDS) pattern and elemental mapping analysis combinatively provided evidences for the existence of ZnO NPs in the SBA-15 support. Fig. 4 shows the typical wheat-like macrostructures type morphology of SBA-15 [18,27]. The EDS spectra Fig. 4 (c) confirmed the presence of O, Si and Zn while EDS mapping analysis of the selected rectangle in Fig. 4 (d) shows the uniform dispersion of Zn in the ZnO@SBA-15. From the wide angle XRD diffraction data, the sole presence of pure, highly crystalline ZnO in SBA-15 is confirmed so the Zn detected the EDS patterns must be ZnO NPs. Moreover, the Zn content in the ZnO@SBA-15 was obtained from the EDS analysis (2.18 wt%) and so the amount of ZnO can be calculated from the Zn content (2.70 wt%).

FT-IR spectra of SBA-15 and ZnO@SBA-15 materials are illustrated in Fig. 5. The broad band appeared around 3800-3000 cm\(^{-1}\) and 1635 cm\(^{-1}\) corresponds to O-H stretching and bending vibration respectively which associated with the surface hydroxyl groups and adsorbed water molecules of SBA-15 [28]. The typical
Si-O-Si bands associated with the formation of a condensed silica network appeared around 1260-1000, 807, 463 cm\(^{-1}\). The weak peak associated with the noncondensed Si-OH groups is observed at 960 cm\(^{-1}\) [28]. In case of ZnO@SBA-15, the peak due to Zn-O stretching vibration merge with the peak at 463 cm\(^{-1}\) of Si-O-Si bands that result in the broadening of this peak [21a]. Moreover, the peak associated with the uncondensed Si-OH groups was diminished due to presence ZnO NPs in the surface of SBA-15. Besides these, all other peaks corresponds to SBA-15 are also present in ZnO@SBA-15.

The UV-vis absorption spectra of the ZnO NPs supported on SBA-15 is depicted in Fig. 6. The ZnO NPs shows a band in the ultraviolet region and the \(\lambda_{\text{max}}\) is observed at 373 nm [24]. Based on the maximum absorption wavelength, the band gap of ZnO NPs is calculated to be 3.32 eV according to the relation \(E_{\text{bg}} = \frac{1240}{\lambda_{\text{max}}}[29]\). Herein, we have demonstrated the catalytic activity of ZnO@SBA-15 nanocomposite material for Biginelli condensation reaction with a low catalyst loading and shorter reaction time than unsupported ZnO NPs [17c]. In order to develop a suitable reaction protocol, we have performed the aforementioned reaction by varying the reaction parameters such as solvent, amount of catalyst, amount of urea, temperature and time. Since ethanol is the most widely used solvent for Biginelli reaction, so using ethanol as solvent and taking the reaction of benzaldehyde, ethyl acetoacetate and urea as model reaction, the optimum amount of catalyst, urea,
temperature and time was investigated. By systematically taking the reaction condition, we have been able to get maximum 96% isolated yield for the aforementioned model reaction (Table 1, entry 11). Furthermore, the effect of increasing or decreasing reaction parameter is illustrated in Fig. S3, ESI.

It can be seen that increase in catalyst loading beyond 20 mg resulted in decrease of isolated yield as some of the products may adsorb on the active catalytic sites thereby decreasing active sites for reagent to be adsorbed [Fig. S3 (a), ESI]. For the Biginelli reaction, always excess urea is taken, so a study of the amount of urea is also needed to be done. Here, we have found maximum 1.4 mmol urea needed to use to obtain maximum isolated yield for our model reaction. Further increase in amount of urea did not increase the isolated yield [Fig. S3 (b), ESI]. The study of the effect of temperature is always crucial for Biginelli reaction as a high temperature is needed for activation of the catalyst. Here we have obtained maximum isolated yield at 65°C, no increase in isolated yield is observed after increasing reaction temperature beyond 65°C [Fig. S3 (c), ESI]. The isolated yield of the reaction is increased with the reaction time and the optimum reaction time needed for our model reaction is 150 min [Fig. S3 (d), ESI]. In the solvent compatibility study, ethanol (Table 1, entry 2) was found to be the most suitable solvent for the aforementioned model reaction. In case water as solvent low yield was obtained (Table 1, entry 2) while a mixture ethanol/water produced good yield (Table 1, entry 4). Other solvent system such as methanol, acetonitrile produces excellent yields (Table 1, entries 5,6) but chloroform, ethyl acetate, toluene and THF produces very low yield (Table 1, entries 7–10). However solvent-free condition resulted 57% isolated yield (Table 1, entry 11).

The blank reaction without the catalyst was carried out in ethanol but did not produce any desired product (Table 1, entry 3). Solvent optimization was performed to find out the best solvent under the suitable reaction condition (Table 2).

A hot filtration test was carried out to check that the catalytic activity was originated from the ZnO NPs embedded in the SBA-15 support and not from leached ZnO NPs to the reaction mixture. For this test, the Biginelli condensation reaction among benzaldehyde, ethyl acetoacetate and urea was carried out at 65°C for 90 min in presence of the ZnO@SBA-15 catalyst following aforementioned procedure in the experimental section. At this stage the 70% isolated yield of the product was obtained. The catalyst was then filtered off under hot conditions and with the filtrate the reaction was continued for another 60 min at the same reaction temperature as the optimum time required for this reaction is 150 min. But no increase in isolated yield of the product beyond 70% was observed. Furthermore, the Zn content in the ZnO@SBA-15 catalyst before reaction was 2.51 wt% from the AAS analysis. But for the ZnO@SBA-15 catalyst separated during hot filtration test the Zn content was marginally decreased to 2.49 wt% (this decrease is

![UV-Vis absorption spectra of as-synthesized ZnO@SBA-15 nanocomposite material.](image)

**Table 1**

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<tr>
<th>Entry</th>
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<th>Time (min)</th>
<th>Isolated yield (%)</th>
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<td>75</td>
<td>150</td>
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The data in bold in the table means maximum isolated yield obtained in the best optimized condition for the reaction.

a Reagent and reaction condition: benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.4 mmol), 20 mg ZnO@SBA-15 catalyst (3.12 wt% ZnO), ethanol (2 mL), temp (°C), time (min).

b Isolated yields are based on benzaldehyde.
within the experimental error). These experimental results confirmed the heterogeneity as well as leach-resistant characteristics of ZnO NPs from the SBA-15 support in our present reaction protocol for Biginelli condensation reaction.

Reusability is a must needed criterion for any heterogeneous catalyst. The stability and reusability study of the recovered ZnO@SBA-15 catalyst after the fresh run was studied for another four times for the reaction of benzaldehyde, ethylacetoacetate and urea. The reaction was carried out according to the mentioned procedure in the experimental section. After each run, the catalyst was washed with acetone and ethanol several times, dried at 60°C and used for next run. The 1st run is for the fresh catalyst and about 96% isolated yield was obtained (Fig. 7). In the 2nd run which is for the recovered catalyst showed a little decrease in isolated yield but after that the isolated yield was maintained at almost 90%. Moreover, the wide angle XRD data and TEM image of the recovered catalyst after 5th run confirmed the stability of the catalyst. Furthermore, no Zn was detected in washing solution of the catalyst by AAS analysis. All these experimental evidences supported the stability, heterogeneity and leach-resistant characteristics of the as-synthesized ZnO@SBA-15 nanocomposite catalyst.

Further validation of our ZnO@SBA-15 catalyst was done by carrying out the Biginelli reaction for unsupported ZnO nanopowder. Here, we have taken benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.4 mmol), 25 mg ZnO nanopowder as catalyst and employed the same aforesaid procedure for Biginelli reaction. We have obtained 32% isolated yield for the reaction. The stability of unsupported ZnO nanopowder was tested by studying the recyclability of catalyst for the Biginelli condensation reaction among benzaldehyde, ethylacetoacetate and urea. We employed same reaction conditions as ZnO@SBA-15 catalyst for this study and observed that unlike ZnO@SBA-15 catalyst, isolated yield decreases continuously in each run probably due to the aggregation of the unsupported ZnO nanopowder in the Biginelli reaction condition.

To explore the scope of our reaction protocol, various aldehyde with electron donating and electron withdrawing group, ethyl or methyl acetoacetate and urea or thiourea were employed as substrates and a diverse range of dihydropyrimidinones (DHPMs) and thione derivatives were synthesized (Table 3). For reaction among aldehyde with electron donating and electron withdrawing group, ethyl acetoacetate and urea or thiourea were employed as substrates and a diverse range of dihydropyrimidinones (DHPMs) and thione derivatives were synthesized (Table 3). For reaction among various substituted aldehyde, methyl acetoacetate and urea also afforded good to excellent yield (Table 3, entries 1–8). On the other hand, reaction among various substituted aldehyde, methyl acetoacetate and urea also afforded good to excellent yield (Table 3, entries 9–12) but somewhat lesser than when ethyl acetoacetate as one of the Biginelli substrate. More importantly, for thiourea, the reaction protocol afforded excellent yield (Table 3, entries 13–16) as sulphur containing Biginelli products have specific biological activity.

On the basis of our experimental evidences (spectroscopic data of some selected products is mentioned in ESI) and previously reported research work, a plausible catalytic cycle for the Biginelli condensation reaction over ZnO@SBA-15 catalyst is depicted in

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<th>Entry</th>
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* Reagent and reaction condition: benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.4 mmol), 20 mg ZnO@SBA-15 catalyst (3.12 wt% ZnO), solvent (2 mL), 65°C, 150 min.
* Isolated yields are based on benzaldehyde.
* No catalyst.
Scheme 1. In the proposed catalytic cycle, the reaction starts with the attack of activated of a β-ketoester (A) to an activated aldehyde (B), so as to form the Knoevenagel condensation adduct C. The adduct C undergoes elimination of an H₂O molecule to give a α,β-conjugated enone D. This intermediate D is attacked by an –NH₂ group of a urea or thiourea molecule termed as E, which gives another intermediate F. An intramolecular attack of the remaining –NH₂ group of the urea or thiourea on the neighboring carbonyl group within intermediate F generates a six-membered intermediate G. The intermediate G, which finally regenerates the ZnO@SBA-15 nanocomposite catalyst and gives the Biginelli product with elimination of an H₂O molecule.

4. Conclusions

Herein, we have synthesized and characterized a new ZnO@SBA-15 nanocomposite material. The as-synthesized ZnO@SBA-15 nanocomposite exhibited enhanced catalytic activity for three component Biginelli condensation reaction to afford desired DHPM products in good to excellent yields. This new ZnO@SBA-15 nanocomposite catalyst has several notable features such as high surface area, well dispersed ZnO NPs with a narrow distribution compared to neat unsupported ZnO NPs. These features are crucial for the low catalyst loading and shorter reaction time taken for Biginelli condensation reaction in this work. Moreover, the nanocomposite catalyst also displayed excellent stability, recyclability and leach-resistant behaviour. The Biginelli condensation is an acid-demanding reaction so our ZnO@SBA-15 nanocomposite catalyst may also show catalytic activity for other acid-demanding organic reactions. As ZnO nanocatalyst shows photocatalytic activity and activity depends on the method of synthesis so this nanocomposite will also be useful as photocatalyst for degradation of hazardous organic dye pollutants.

Table 3
Scope of the ZnO@SBA-15 catalyst for synthesis of various DHPMs via Biginelli condensation reaction. a

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<td>89%</td>
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<td>150 min</td>
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a Reagent and reaction condition: aldehyde (1 mmol), ethyl or methyl acetoacetate (1 mmol), urea or thiourea (1.4 mmol), 20 mg ZnO@SBA-15 catalyst (3.12 wt% ZnO), ethanol (2 mL), 65 °C. Isolated yields are based on aldehyde.
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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.micromeso.2017.06.052.

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