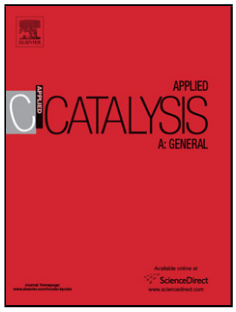

Title: Keggin type phosphotungstic acid encapsulated Chromium (III) Terephthalate Metal Organic Framework as active catalyst for Biginelli condensation

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PII: S0926-860X(15)00326-9
DOI: http://dx.doi.org/doi:10.1016/j.apcata.2015.05.021
Reference: APCATA 15395

To appear in: *Applied Catalysis A: General*

Received date: 7-3-2015
Revised date: 9-5-2015
Accepted date: 16-5-2015

Please cite this article as: M. Saikia, D. Bhuyan, L. Saikia, Keggin type phosphotungstic acid encapsulated Chromium (III) Terephthalate Metal Organic Framework as active catalyst for Biginelli condensation, *Applied Catalysis A, General* (2015), http://dx.doi.org/10.1016/j.apcata.2015.05.021

Highlights:

- The Biginelli reaction was studied.
- Heteropoly acid $H_3PW_{12}O_{40}$ (PW) encapsulated into MIL101 was used as catalyst.
- Effect of MIL-101 on catalytic behaviour of PW was demonstrated.
- The catalyst is easily recoverable and reusable without much change in activity.

Keggin type phosphotungstic acid encapsulated Chromium (III) Terephthalate Metal Organic Framework as active catalyst for Biginelli condensation

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Abstract

Keggin- type phosphotungstic acid ($H_3PW_{12}O_{40}$, PTA) encapsulated in the mesocages of chromium-based terephthalate metal-organic framework (MIL-101) was established to be an active heterogeneous catalyst for three component Biginelli condensation reaction with excellent yields(75-90%) and selectivity under solvent free condition. Here phosphotungstic acid can effectively incorporated into the matrix of MIL-101 by an impregnation method. The synthesized PTA@MIL-101 was characterized by employing various spectroscopic techniques as well as different analytical methods. Moreover, the catalyst could easily be recovered and recycled without any significant loss of its catalytic activity.

Keywords: PTA@MIL-101; Impregnation, Biginelli condensation

1. Introduction

Nowadays multicomponent reaction has become a remarkable area of research, particularly in organic chemistry [1] as these reactions surpass the atom economy of the process. These reactions are key source of molecular diversity which makes them powerful tool in modern drug discovery processes. Furthermore, the one-pot character furnishes fewer by-products in comparison to classical stepwise synthetic route with lower cost, time and energy. Among the multicomponent reactions, Biginelli reaction is one of the most studied reactions since the product of this reaction is Dihydropyrimidinones (DHPMs) which are vital medicinal synthones that display a wide range of biological activities such as antibacterial, anti-inflammatory, antiviral, anti-tumour [2-4]. A large number of dihydropyrimidinones derivatives are pharmacologically important as antagonists, antihypertensive agents, significant calcium channel blockers, and neuropeptide antagonists [5-10]. Additionally, several marine alkaloids involving the DHPM core unit, such as batzelladine alkaloids possess certain biological properties which are of great significance.

Various classical methods are available for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones employing Lewis acids such as $BF_3 \cdot Et_2O$ and $Sr(NO_3)_2$, ceric ammonium nitrate [11,12,13]. Heteropolyacids are also use as an acid catalyst for this transformation [14]. However, the difficulties with polyoxometalates are their recovery and reuse in presence of water and organic solvents [15,16]. To overwhelm this shortcoming, heterogenisation of these polyoxometalates into various host supports like silica [17], activated carbon [18] and zeolites [19] has already been reported. Nevertheless, these supported catalyst tend to have restricted POM loading, show some leaching and susceptible for agglomeration [20].

MIL-101(Materials of the Institut Lavoisier no. 101) is mesoporous metal-organic framework, has mesosize cages of 2.9 and 3.4 nm with two microporous windows of 1.2 and 1.6 nm respectively[21-22], resulting a high surface area that make this MOF an attractive host for the encapsulation of polyoxometalates. Moreover, supporting phosphotungstic acid in the host lattice structure of metal-organic framework provide many advantages like improving the molecular accessibility by isolating the individual keggin units as compared to its bulk counterpart which has relatively low surface area($<10\ m^2g^{-1}$), facile catalyst recovery and recycling etc. Several attempts have been made for encapsulating polyoxometalates into the matrix of metal-organic framework [23-34]. These phosphotungstic acids encapsulated into MIL-101 exhibits good catalytic performance in the esterification reaction of *n*-butanol with acetic acid in the liquid phase [24], Knoevenagel condensation [24], oxidative desulfurization[29], selective oxidation of alkenes with aqueous hydrogen peroxide[30], hydrolysis and esterification reaction [33], selective dehydration of fructose and glucose to 5-hydroxymethylfurfural [34], aldehyde-alcohol reactions [36], etc. Like MIL-101, $Cu_3(BTC)_2$(HKUST-1) is also a potential metal-organic framework for successful incorporation of keggin type phosphotungstic acids. L.H. Wee and his co-workers synthesized $Cu_3(BTC)_2$ encapsulated Keggin heteropolyacid nanomaterial and investigate its catalytic activity in acid catalyzed esterification reaction [23] [32]. Micek-Ilnicka et al. synthesized a hybrid material of tungsten heteropolyacid (HPW) and iron-based MOF Basolite™ F 300 and demonstrate the influence of acid particles distribution on ethanol conversion in hybrid materials [27]. Keeping that in mind, we have synthesized a hybrid material of phosphotungstic acid with MIL-101 through an impregnation technique [37] and studied its catalytic activity in Biginelli reaction under solvent free condition. The catalyst is easily recoverable and reused up to three times without significant loss of its activity. Hence, short

reaction time, facile recovery and recycling of the catalyst and solvent free condition makes our process more advantageous to that of the other processes.

2. Experimental

2.1 Synthesis of MIL-101

MIL-101 was prepared according to the reported method by Férey et al[1]. involving hydrothermal treatment of a mixture of 3mmol of $Cr(NO_3)_3 \cdot 9H_2O$, 3mmol of terephthalic acid (H_2bdc) and 0.6ml of 5M HF (3mmol) in 15ml H_2O at 220^0C for 8h in a Teflon-lined autoclave bomb. After equilibration at ambient temperature, the resulting Cr-MIL-101 solid was filtered to remove the unreacted colourless crystals of H_2bdc and purified by double treatment with DMF at 60^0C for 3h and then triple treatment with ethanol at 70^0C for 2.5h. Finally the green solid was separated by centrifugation, dried in an air oven at 70^0C overnight and kept it in a vacuum desiccator.

2.2 Synthesis of PTA@MIL-101

1 g of dry MIL-101 was added to an aqueous solution of phosphotungstic acid (0.6g dissolved in 20ml of distilled water). The resulting suspension was sonicated and stirring at room temperature for 48h. The solids were separated by centrifugation, repeatedly washed by methanol and water and dried under vacuum. The W content (10wt %) in the synthesized material has been calculated from AAS technique.

2.3 General procedure for the one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones

A solution of ethylacetoacetate (1 mmol), aldehyde (1 mmol) and urea (1.5 mmol) was heated to 100^0 C under solvent-free condition in the presence of PTA@MIL-101 (0.6 mol%). The progress of the reaction was monitored through TLC. After completion, the reaction mixture was cooled to room temperature, dissolved in ethanol and filtered to separate the catalyst. The ethanol was evaporated in rotavapor and the crude product was poured into crushed ice with thorough stirring for 10 min. The solid product was filtered and further purified by re-crystallization from n-hexane/ethyl acetate(3:1), to afford pure 3,4-dihydropyrimidin -2(1H)-ones. The products were characterized by (^{1}H, ^{13}C) NMR spectroscopy and all give satisfactory results (ESI).

3. Results and Discussion

Metal-organic framework like MIL-101 is a robust material with mesoporous cages that possesses high surface area as well as high hydrothermal stability. These features make this MOF a good candidate as catalyst support [38] for various important organic transformations. The MOF is synthesized by following the reported method by Férey et al.

and phosphotungsic acid was incorporated in its matrix by a simple impregnation method. The resulting PTA@MIL-101 was thoroughly characterized with the help of different analytical techniques like PXRD, FT-IR, N_2 physisorption, ^{31}P Solid state MAS NMR, NH_3-TPD, XPS and FESEM analysis. The PXRD pattern of the composite PTA@MIL-101 possesses notable changes in the diffraction patterns after incorporation of PTA in MIL-101. Characteristic diffraction peaks appears between 2θ (6-8^o) of the composite materials (Fig 1(b)) in comparison to the parent material (Fig 1(a)) clearly demonstrated the ordered assembly of PTA molecules into the cages of MIL-101 [23]. This ordered encapsulation of heteropoly acid increases the stability of MIL-101 as indicated by the thermogravimetric study (ESI, Fig S2). However, no reflection peak characteristic of bulk PTA is observed, establishing the well dispersion of PTA molecules in the mesocages of MIL-101.

The FESEM images of MIL-101 and PTA@MIL-101 is shown in (ESI, Fig.S3 (a), (b)). It is seen that phosphotungstic acid incorporates on MIL-101 surface without fragmenting the characteristic cubic symmetry of parent MIL-101. TEM images of the composites (ESI, Fig S4) retained the overall octahedral shape of the autoclaved MIL-101 particles although the shape was slightly less well defined, because of the extended exposure of the MIL-101 to water in the process of impregnation. The elemental mapping (Fig.2) of different elements clearly demonstrate the well distribution of phosphotungstic acid in the mesocages of MIL-101.

The specific surface area of the composite material was measured by N_2 physisorption analysis at 77K (Fig.4(a)). The BET surface area and pore volume of PTA@MIL-101 was found to be lower than that of the pristine MIL -101 which is supposed to be filling of the pore space of the support by the heavy heteropolyacid molecules. In spite of that, significant BET surface area and pore volume of 1032 m^2g^{-1} and 0.61cm^3g^{-1} were retained. The differential pore volume versus pore diameter plot, i.e. BJH plot, (ESI, Fig.S5) shows the uniform pore distribution of the support after encapsulation of the heteropoly acid molecules. FT-IR analysis of the composite material (Fig. 3(b)) shows the characteristic bands at 828, 903 ν(W-O-W), 983 ν(W=O) and 1080 cm^{-1} ν(P-O), confirming the incorporation of Keggin HPW in MIL-101[38,39]. The ^{31}P solid-state MAS NMR (Fig.3(c)) exhibit a single signal at -15.4 ppm which clearly indicates the stability of Keggin polyoxometal anion within the cages of MIL-101. XPS spectrum of PTA@MIL-101 reveals the presence of phosphotungstic acid within the framework of MIL-101(ESI, Fig. S1)

The acidity of the PTA@MIL-101 has measured through Temperature- programmed desorption (TPD) of ammonia. In the NH_3-TPD profile (ESI, Fig S6) the desorption peak positioned at low temperature 233^oC can be designated to NH_3 adsorbed on the open metal sites of MIL-101 [39]. The signal appeared at higher temperature (667^oC) may be attributed to the ammonium salt of heteropoly acids [40]. The position of the peak at higher temperature is shifted as compared to that of the neat phosphotungstic acid may be owing to the incorporation of phosphotungstic acid to the matrix of the parent MOF [38]. The total amount of acidic sites on the synthesized PTA@MIL-101 as determined from the NH_3-TPD was found to be 0.288 mmol g^{-1}.

The condensation reaction between aldehydes, 1,3-dicarbonyl compounds and urea or thiourea catalyzed by phosphotungstic acid, an environmentally benign solid protic acid under solvent free condition is an important organic transformation as the products of the reaction are of biological importance. In our present protocol, the three component condensation reaction between benzaldehyde, ethylacetoacetate and urea was carried at 100^oC using PTA@MIL-101 as catalyst under solvent free condition. This protocol gives good yield of the products. The problems associated with using solvent such as cost, safety, and handling are also examined. Furthermore, under solvent free condition, the reactivity increases which results in the decrease of the reaction time. The use of the parent MIL-101 gave essentially no required product in this reaction system, confirming as anticipated the need of phosphotungstic acid moiety to perform the condensation reaction. The incorporation of phosphotungstic acid significantly enhances the reaction.

In order to monitor the catalytic efficiency of the heterogeneous PTA@MIL-101 catalytic system, we were carried out the same reaction in the presence of PTA@MIL-101 containing different PTA loading. Results of the reaction (Table.1) pointed to an optimized performance of 0.6 mol% of PTA@MIL-101, which selectively furnish the corresponding 3,4-dihydropyrimidin-2(1H)-one in 90% yield at 100^oC under solvent-free condition after 1h. With increases in the amount of catalyst, i.e. for 0.9 mol% (Table.1, entry 4) resulted in the declining of the product yield due to the internal diffusion limitations inside the porous catalyst [41].

The potency of the reaction was influenced by temperature. Results of the reaction between benzaldehyde, ethylacetoacetate and urea are summarized in (Table. 2). The yield of the reaction was low below 80^oC (Table. 2, entry 2) where increasing temperature from 90-

130^{o}C (Table.2, entry 3, 4) had insignificant effect on the yield%. Taking all these aspects 100^{0}C temperature was selected for all the further studies.

The dimension of the presented catalyst system was then subsequently extended to the different substituted aromatic aldehydes with electron withdrawing and electron releasing substituents on the phenyl ring using the optimum PTA@MIL-101 catalyst. The results summarized in (Table. 3), shows that PTA@MIL-101 was extremely active for all the substrates of benzaldehydes including methylacetoacetate(Table. 3, entry 9, 10, 11, and 12) and more importantly thiourea (Table. 3, entry 13, 14 and 15) that provide dihydropyrimidin-2 (1H)-thiones which are of much concern relevant to biological activity indicating a high flexibility of the MOF supported phosphotungstic acid catalyst.

The advantages of this present protocol over some reported methods were short reaction time, solvent free reaction condition, catalyst recovery etc. From the catalysis point of view we have selected the three component condensation reaction of urea, ethylacetoacetate, and 4-nitrobenzaldehyde as a model reaction and make a comparison of our results with that of the reported one (ESI, Table S1). Our catalyst is superior on the basis of mol% of the catalyst as well as the time required for the chemical transformation.

A plausible mechanism (Scheme 1) was proposed based on available literature and our experimental report. The reaction was proceed by imine formation from aldehyde and urea or thiourea followed by the addition of enol tautomer of 1,3- dicarbonyl compounds to the imine. The final step of the reaction is the cyclodehydration of ureide to afford the corresponding dihydropyrimidin-2(1H)-one. Here PTA@MIL-101 acts as a proton source which enhances the progress of the reaction by enolizing the 1,3-dicarbonyl compounds to enolate intermediate and dehydrating the ureide. The support, due to its high surface area provides not only better dispersion for the phosphotungstic acid, the active sites of the reaction but also make a facile recovery of the catalyst from the reaction medium.

The heterogeneous nature of PTA@MIL-101 was confirmed by performing leachability study of phosphotungstic acid from the support. A hot filtration test was carried out by taking the reaction between ethylacetoacetate, benzaldehyde and urea as the model reaction (detail procedure is in the supporting information). After 20 minute of the reaction the isolated product yield was found to be 35%. No further increased in the yield beyond 40% is observed after 60 minute of the reaction. The increase in the isolated product yield from 35% to 40% may be due to the slight leaching of the phosphotungstic acid moiety from the support.

For the interest of environmental friendly procedure, the reuse of the catalyst is more desirable. The recyclability of the PTA@MIL-101 catalyst was examined in the condensation of benzaldehyde, ethylacetoacetate and urea under the optimized conditions. After the catalytic reaction, the catalyst was washed with ethanol, then with acetone, and dried at 100^0C for 3h. The catalyst is then reutilized in subsequent runs under identical reaction condition. The results included in the plot (Fig.4) shows that there was no loss in efficiency of the catalyst up to three runs. FT-IR study of the recovered catalyst (Fig 3(b)) is also in good agreement with this result. The peaks around 800-1100 cm^{-1} clearly established the conservation of keggin structure of the heteropoly acid. The FESEM image of the recovered catalyst (ESI, Fig S3 (C)) displays the preservation of the integrity of parent material. These experimental results recommend that all the reactions are part of a heterogeneous process and also reveal the robustness of the catalyst.

4. Conclusion

In summary, PTA encapsulated MIL-101 have been synthesized using the simple impregnation approach. The obtained catalyst exhibited excellent activity for the solvent free synthesis of various bioactive 3,4-dihydropyrimidin-2(1H)-ones through Biginelli reaction of benzaldehyde, urea and ethylacetoacetate. Additionally, the catalyst is easily recoverable and can be reused without notable change in its catalytic activity. The support makes an impact of this catalytic transformation by heterogeneized heteropolyacids and facilitated the progress of the reaction. Therefore, facile catalyst recovery, short reaction time as well as recyclability established this heterogeneous catalyst as a potent candidate for this organic transformation and making this methodology economically and environmentally acceptable.

Acknowledgements

The authors are grateful to the Director of CSIR-North East Institute of Science and Technology, Jorhat, Assam, India for his kind permission to publish the work. We are thankful to Dr P. Sengupta, Head of Materials Science Division and Dr D. K. Dutta for support, and non network project MLP-6000(WP-1) and network project (CSC-0408) project for financial assistance. M. S. acknowledges DST New Delhi for an INSPIRE fellowship.

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Captions

Fig. 1 (a) PXRD pattern of MIL-101, (b) PXRD pattern of PTA@MIL-101

Fig.2 EDS mapping of different elements of PTA@MIL-101

Fig.3 (a) N_2 adsorption isotherm of PTA@MIL-101(red), MIL-101(black), (b) FT-IR spectra of recovered PTA@MIL-101(Green), MIL-101(black), PTA@MIL-101(red) and PTA(blue) (c) ^{31}P solid-state MAS spectrum of PTA@MIL-101

Fig. 4 Catalyst recycling test for PTA@MIL-101

Table 1 Effect of catalyst amount.

Table 2 Effect of temperature.

Table 3 PTA@MIL-101 catalyzed Biginelli reaction with different substrates.

Scheme1 Plausible mechanism of Biginelli condensation.

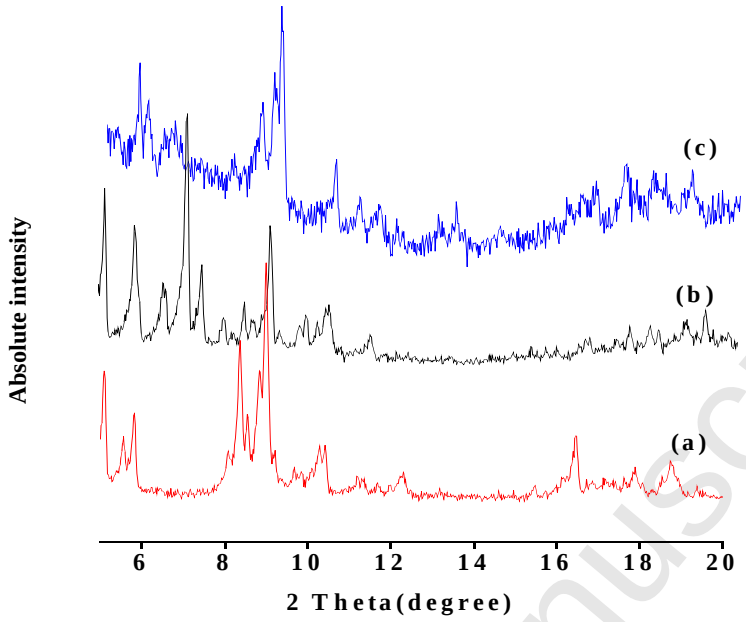


Fig.1 PXRD pattern of (a) MIL-101, (b) PTA@MIL-101, (c) recovered PTA@MIL-101

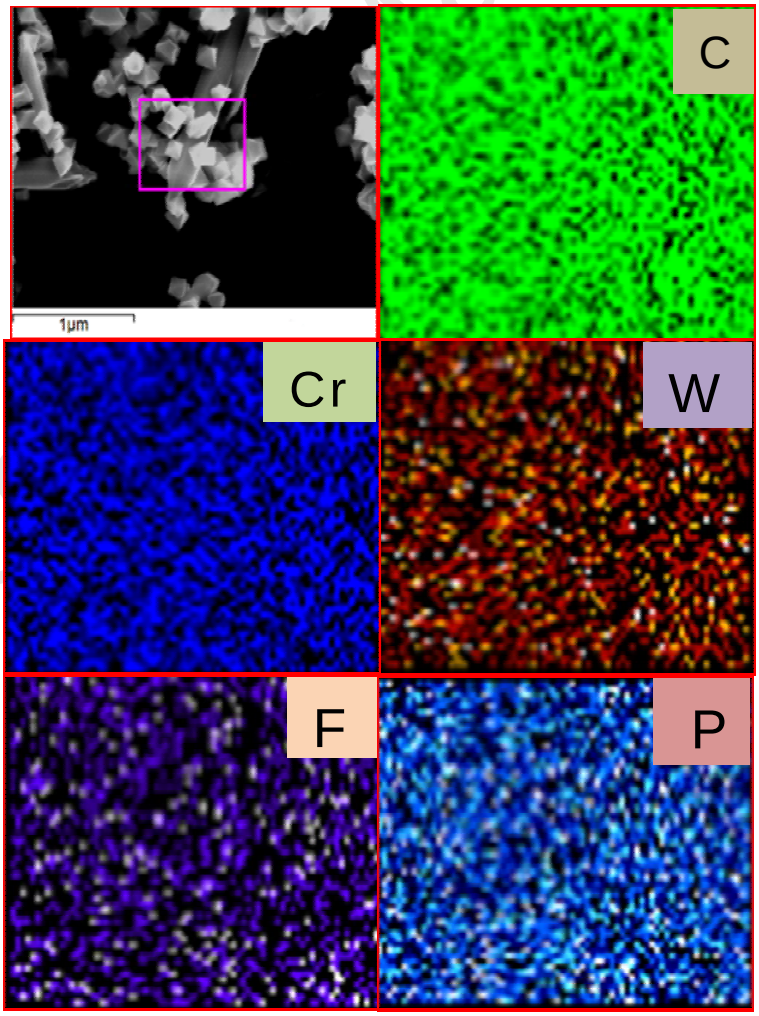


Fig.2 EDS mapping images of different elements of PTA@MIL-101

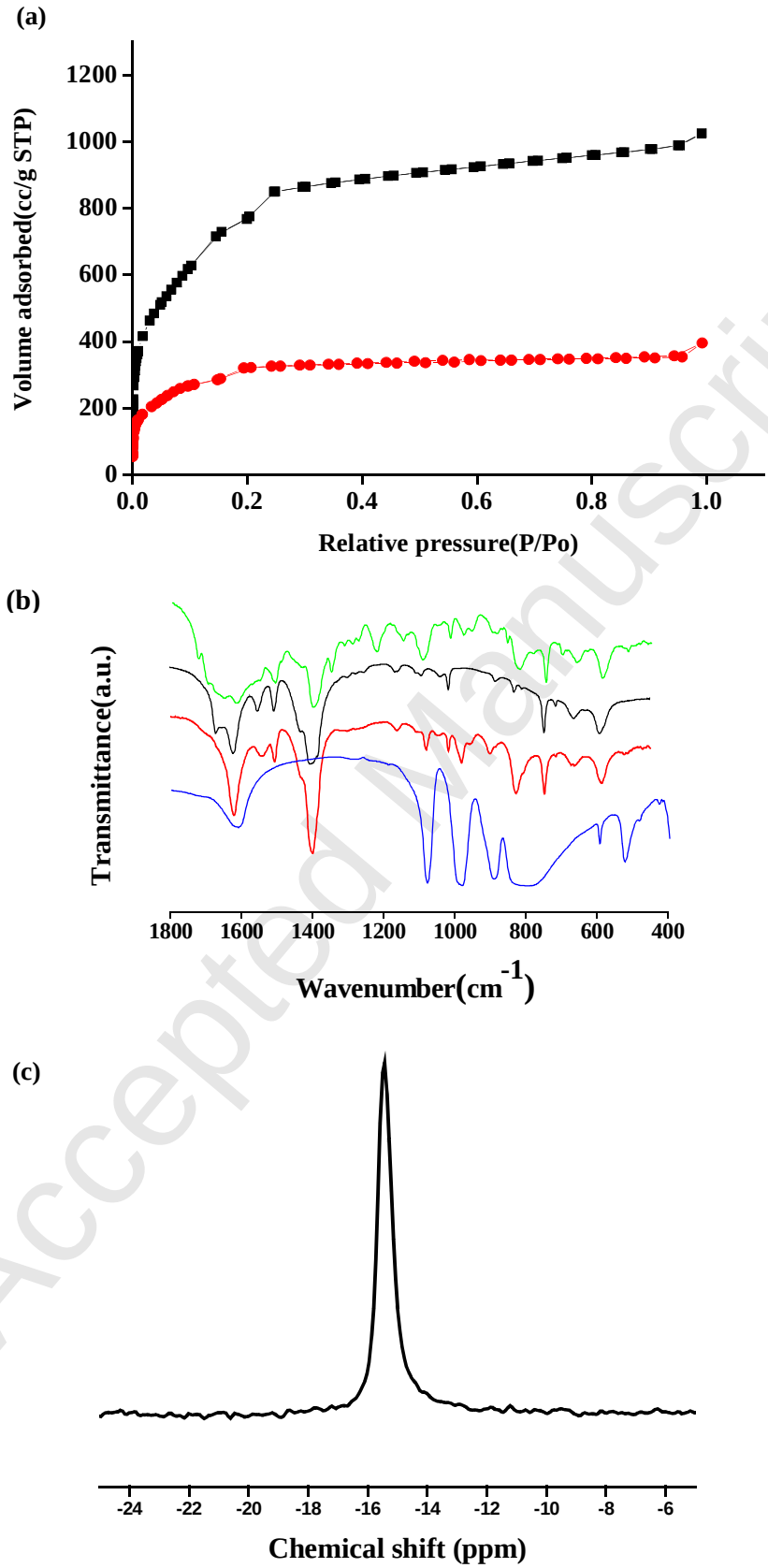


Fig. 3 (a) N_2 adsorption isotherm of MIL-101(Black), PTA@MIL-101(red), (b) FT-IR spectra of recovered PTA@MIL-101(Green), MIL-101(Black), PTA@MIL-101(red) and PTA(blue) (c)^{31}P solid state MAS NMR spectrum of PTA@MIL-101

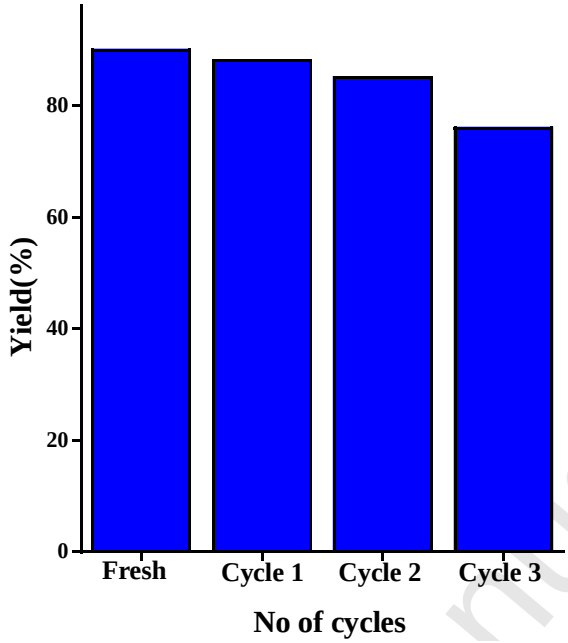


Fig.4 Catalyst recycling test for PTA@MIL-101

Table1: Effect of catalyst amount[a]

Entry	Catalyst amount (mol%)	Yield (%)[b]
1	0.2	50
2	0.4	65
3	0.6	90
4	0.9	82

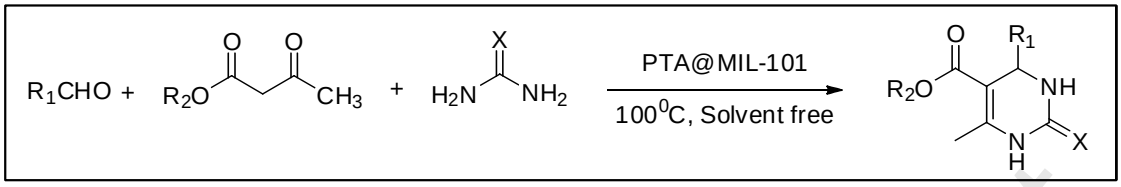
[a]Reaction conditions: benzaldehyde (1mmol), ethylacetoacetate (1mmol), urea (1.5 mmol), temperature= 100^{o}C, time 1h
[b]Isolated yields are based on benzaldehyde

Table2: Effect of temperature[a]

Entry	Temperature(^{0}C)	Yield (%)[b]
1	Room temperature	No desired product
2	75	60
3	90	87
4	130	88
5	100	90

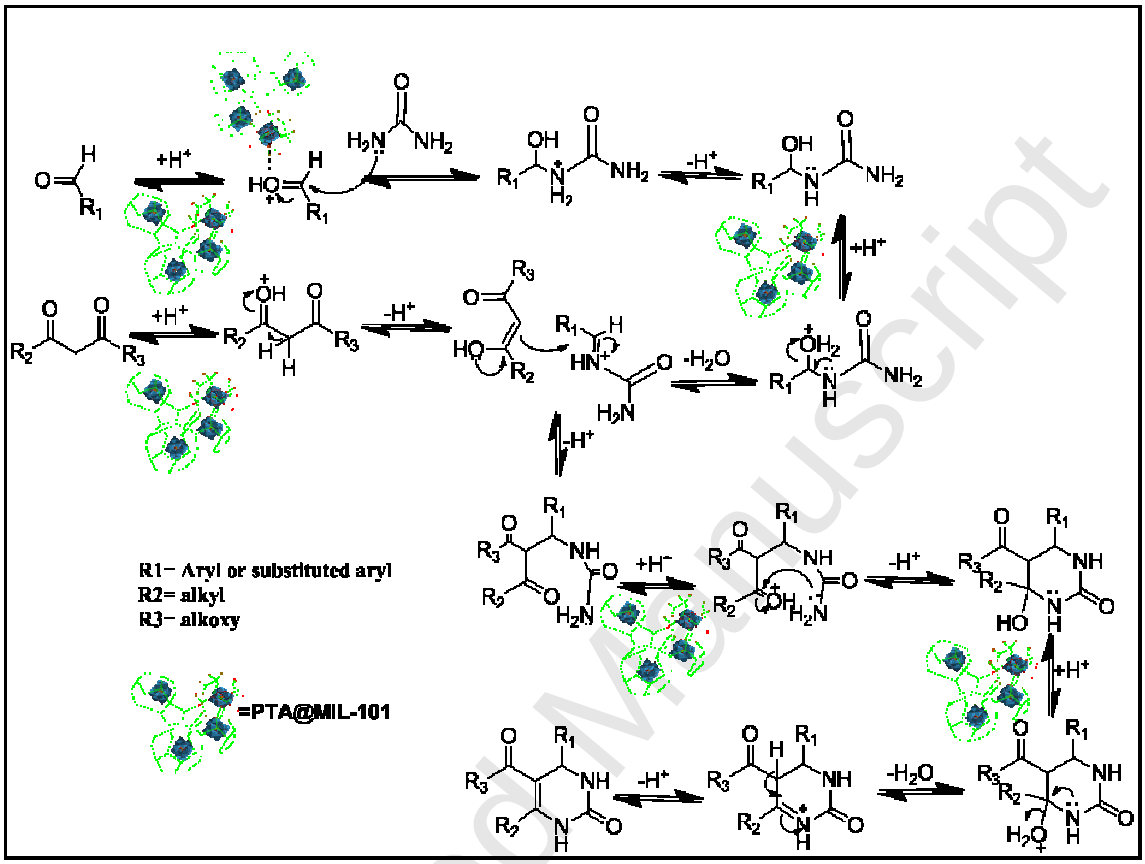
[a]Reaction conditions: benzaldehyde (1mmol), ethylacetoacetate (1mmol), urea (1.5 mmol), PTA@MIL-101= 0.6 mol%, temperature= 100^{o}C, time 1h
[b]Isolated yields are based on benzaldehyde

Table 3: PTA@MIL-101 catalyzed Biginelli reaction with different substrates[a]



Entry	R_1	R_2	X	Time(h)	Yield (%)
1	C_6H_5	$-C_2H_5$	O	1	90
2	4-ClC_6H_5	$-C_2H_5$	O	2	82
3	4-$CH_3C_6H_5$	$-C_2H_5$	O	2	80
4	4-BrC_6H_5	$-C_2H_5$	O	2	83
5	4-$OMeC_6H_5$	$-C_2H_5$	O	2	85
6	4-OHC_6H_5	$-C_2H_5$	O	2	76
7	4-$NO_2C_6H_5$	$-C_2H_5$	O	2	81
8	3-$NO_2C_6H_5$	$-C_2H_5$	O	3	78
9	C_6H_5	$-CH_3$	O	1	82
10	4-$NO_2C_6H_5$	$-CH_3$	O	2	75
11	4-$CH_3C_6H_5$	$-CH_3$	O	2	78
12	4-ClC_6H_5	$-CH_3$	O	2	80
13	C_6H_5	$-C_2H_5$	S	1	80
14	4-ClC_6H_5	$-C_2H_5$	S	2	85
15	4-$CH_3C_6H_5$	$-C_2H_5$	S	2	83

[a]Reaction conditions: Substituted benzaldehyde (1mmol), dicarbonyl compound (1mmol), urea or thiourea (1.5 mmol), PTA@MIL-101(0.6 mol%).[b] Isolated yields are based on aldehyde. All compounds have been characterized by ^1H and ^{13}C NMR (available in the ESI)



Scheme:1 Plausible mechanism of Biginelli condensation

Graphical abstract

Keggin type phosphotungstic acid encapsulated Chromium (III) Terephthalate Metal Organic Framework as active catalyst for Biginelli condensation

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