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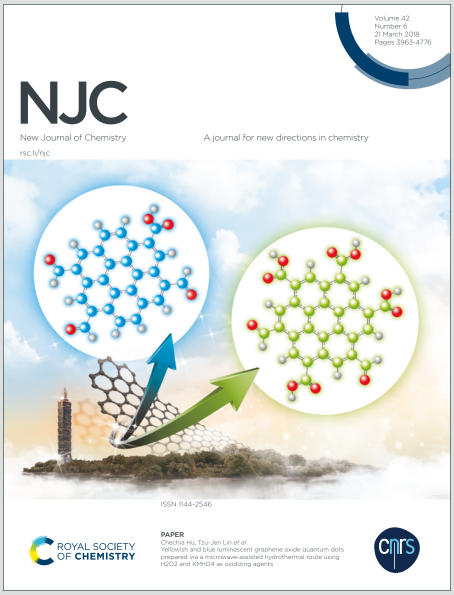

Volume 42
Number 6
21 March 2018
Pages 3963-4776

NJC
New Journal of Chemistry
A journal for new directions in chemistry
rsc.li/njc

ISSN 1144-2546

ROYAL SOCIETY OF CHEMISTRY

PAPER
Chechia Hu, Tzu-Jen Lin *et al.*
Yellowish and blue luminescent graphene oxide quantum dots prepared via a microwave-assisted hydrothermal route using H2O2 and KMnO4 as oxidizing agents

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Journal Name

ARTICLE

Catalytic Conversions of Isocyanate to Urea and Glucose to Levulinate Esters over Mesoporous α-$Ti(HPO_4)_2$. H_2O in Green Media

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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We have described a facile solvothermal synthesis of a sheet-like α-$Ti(HPO_4)_2$. H_2O nanomaterial. The material holds 10.7 nm nanoparticles along with ordered mesopores throughout its hexagonal building blocks. The material possesses 3.86 eV bandgap energy and works as an efficient catalyst for the selective synthesis of ureas from a broad range of isocyanates in presence of H_2O at room temperature with high product yield (up to 93%) and TOF value up to 15.25 h^{-1}. The α-$Ti(HPO_4)_2$. H_2O nanomaterial also catalytically converts glucose to levulinic acid (LA) and subsequently LA to alkyl levulinates in presence of different alcohols with high product yield (up to 98%) and TOF value up to 43.00 h^{-1}. Furthermore, all the reactions are performed in green and facile catalytic conditions without using any hazardous solvent. The α-$Ti(HPO_4)_2$. H_2O catalyst material is also found to be reusable for manifold cycles for all the reactions keeping its catalytic efficiency along with its structural and morphological characteristics unaffected, supporting its industrial relevance.
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Introduction

Phosphate materials with two dimensional open layered framework and mesoscopic void spaces have attracted interest of researchers as they can be widely used in general catalysis[1] as well as photocatalysis,[2] cosmetic production,[3] adsorption[4] and solar cells[5]. Among them, titanium phosphates having compositional and crystal structure diversity is a well-known material. The modified synthetic methods and applications of this material in the generation of value-added chemicals are still to be explored by researchers.

Urea synthesis is one of the most significant organic transformations in recent days because of its extensive applicability in pharmaceutical, agrochemical and petrochemical industries.[6] In conventional way, urea synthesis is done by amines reacting with phosgene,[7] and its derivatives,[8] carbonyl-imidazoles,[9] or CO[10a]/CO_2[10b] using costly metal or non-metal based catalysts. It is important to notice that phosgene is a toxic and environmentally hazardous material. Recently, G. C. Paul et al. reported their work on urea synthesis from isocyanates using four-coordinate Co(III) complexes as homogeneous catalysts under sunlight irradiation.[11] The reaction was done in inert (Ar) atmosphere in presence of DCM as solvent. Therefore, synthesis of potential and cost-effective heterogeneous reusable catalyst which can produce urea in more simplified and environmentally benign reaction pathway without using any hazardous solvent or material is still to be explored.

In 21st century, the most challenging issue is to find out an environment friendly replacement of fossil-based energy sources. That is why clean and renewable energy sources attract attention of researchers as a potential substitute. Besides wind and solar, among the renewable energy sources biomass is the most profuse existing raw material in nature in the form of agricultural wastes.[12] Glucose is the most ideal preferred biomass-derived cheap carbohydrate substrate for the production of extensive range of platform chemicals such as levulinic acid (LA), hydroxymethyl furfural (HMF) and furfural. US Department of Energy has identified LA as one of the most promising platform chemicals for the production of new biochemicals and biofuel additives.[13] Potential heterogeneous catalyst for glucose to LA conversion is with industrial relevance is still to be explored. Weingarten et al. reported solid metal phosphate catalysed LA synthesis from glucose at 160 °C for 3 with La yield of 17.3%.[13] Recently, V. Bokade et al. reported levulinic acid (LA) synthesis from glucose using silicon phosphate catalyst in MIBK–water biphasic system with maximum 81% LA yield at 140 °C for 10 h. [14] Those reports suggested that catalysts with acidic sites (Lewis and Brønsted) is essential for glucose to LA conversion.[13, 14] Therefore, solid heterogeneous catalysts containing oxoanions such as $(PO_4)^{3-}$, ($SO_4)^{2-}$, ($ClO_4)^{1-}$ representing strong acidic active sites presence on catalyst surface drag attention of researchers. Varieties of precious commodity chemicals, used as pharmaceuticals, plasticizers, fuel additives etc[15] can be obtained from LA. Among them, alkyl levulinate is one of the most significant commodity chemicals, which can be derived from LA esterification with alcohols. Alkyl levulinate is a sustainable and environmentally benign replacement of gasoline additives like tetraethyl lead.[16] The major shortcoming for the commercial applicability of levulinate esters is its high production cost. Therefore, finding out a potential catalytic pathway to synthesize levulinic acid from biomass, followed by its esterification is expected to shrink the cost with the extra advantage of renewable raw material source.

In this study, we have reported mesoporous titanium phosphate catalyst, synthesized by a simplistic solvothermal method, as a

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Electronic Supplementary Information (ESI) available: Materials, Instrumentation, [1]HNMR of products. See DOI: 10.1039/x0xx00000x

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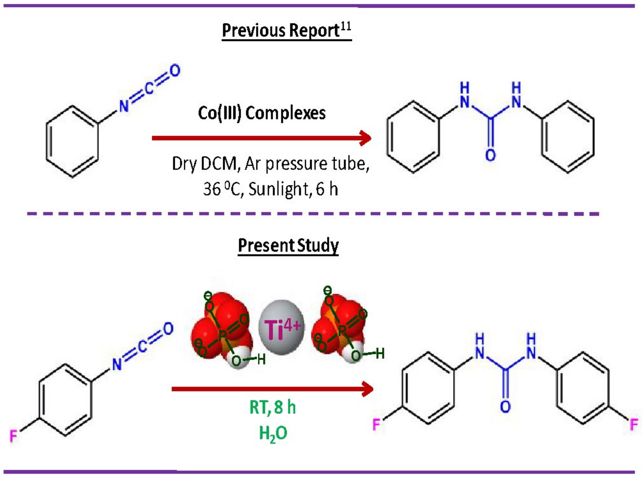
promising low-cost heterogeneous catalyst with wide range of applicability in different industrially important organic transformations such as in urea synthesis from various isocyanate derivatives along with glucose to LA and subsequently LA to levulinate ester synthesis. All the reactions are reported in green and mild reaction conditions without using any hazardous material or solvent with maximum yield upto 93%, 80% and 98% for urea, LA and levulinate ester, respectively. The facile, cost-effective, environment friendly, high productivity and reusable characteristics of the present catalytic system widen its industrial applicability.



Experimental

Synthetic procedure of $Ti(HPO_4)_2.H_2O$ material:

5 mmol of titanium isopropoxide was added in 60 mL ethanol followed by stirring for 30 mins at room temperature. Then, 85% (w/w) phosphoric acid (5 mL) was mixed under continuous stirring, subsequently transferring into 100 mL Teflon-lined autoclave. The autoclave was kept in an oven at 150°C for 1.5 hours. After the reaction, the formed product was gathered by centrifugation, washed with DI water, and dried under vacuum (Figure 1).

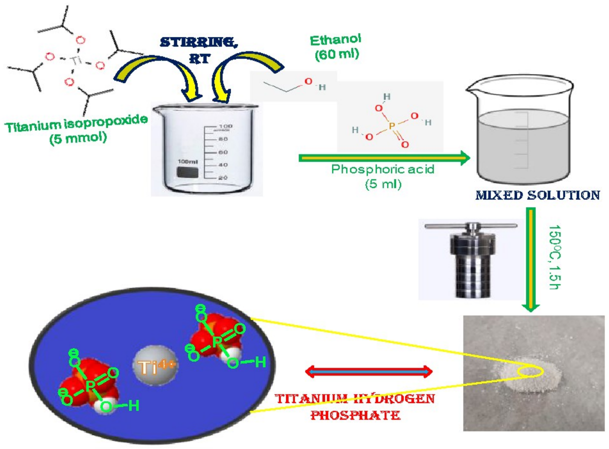


Fig. 1. Synthetic diagram of $Ti(HPO_4)_2.H_2O$ material.

Catalytic activity experiment for conversion of Isocyanate to Urea:

Synthesis of urea was processed in a 25 mL round bottom flask containing a mixture of 5 mmol isocyanate and 10 mg mesoporous $Ti(HPO_4)_2.H_2O$ catalyst in 1 mL H_2O. The reaction was executed for 8 h in green reaction condition at room temperature. After finishing the reaction, the white solid product was isolated and washed with dichloromethane. Pure isolated product was characterized by ^1H NMR spectroscopy.

Catalytic activity experiment for synthesis of levulinic acid (LA) from glucose:

Synthesis of LA from glucose was processed in a 25 mL round bottom flask equipped with a condenser. Te flask was positioned in a temperature controlled oil-bath. The flask contained a mixture of 100 mg glucose, 10 mL DI water as solvent and 30 mg catalyst. The reaction was performed at 120 ⁰C temperature for 8 h. The whole setup was cooled to normal temperature at the end and the catalyst was filtered out. Pure isolated product was characterized by ^1H NMR spectroscopy.

Catalytic activity experiment for conversion of LA to alkyl levulinates :

Esterification reaction of LA was processed in a 25 mL round bottom flask equipped with a condenser. The flask contained a mixture of 5 mmol LA and 3 ml methanol and 15 mg catalyst. The reaction was executed at 70 ⁰C temperature for 2 h. The whole setup was cooled to normal temperature at the end and the catalyst was filtered out and the conversion was tracked through gas chromatography (GC). Pure isolated product was characterized by ^1H NMR spectroscopy.

Results and discussion

Characterization

Powder X-ray diffraction (PXRD) Analysis

The XRD pattern depicted in Fig. 2 confirmed the formation of alpha form of titanium hydrogen phosphate, i.e., α-$Ti(HPO_4)_2.H_2O$ (JCPDS card no. 44-382). There may be an indication of existence of slight amount of amorphousness in the material according to the rough environment of the XRD pattern. The highest intensity peak at 2Θ value 11.4⁰ for the plane (002) having an interlayer gap of 0.76 nm signifies the layered arrangement of the nanomaterial.[17] The crystallite size of the sample was calculated from Scherrer's equation and it was found to be 10.7 nm. From (002) crystal plane using Bragg's equation (nλ = 2dSinθ), the corresponding lattice spacing (d_{002}) value was calculated to be 0.775 nm.

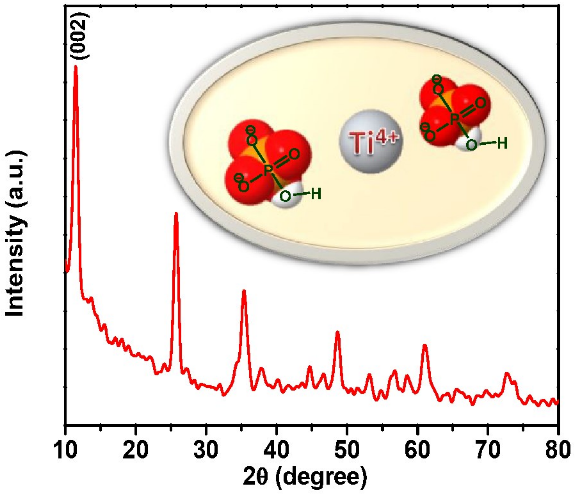


Figure 2. XRD patterns of the sample.

UV-vis analysis

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Figure 3 depicts the UV-visible spectra of the synthesized titanium phosphate sample. It showed a very wide and strong absorption maxima at 251 nm which is due to the electronic transition from O^{2-} 2p to Ti^{4+} 3d orbital.[17] The band gap energy (E_g) is calculated to be 3.86 eV from the absorption edge wavelength (λ), using the formula, E_g (eV)= 1240/λ (nm).[18]

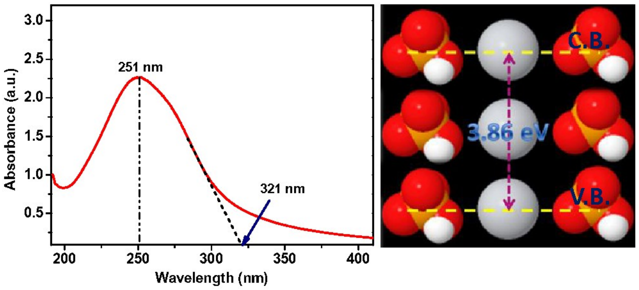


Figure 3. UV-visible absorbance spectra of $Ti(HPO_4)_2.H_2O$ sample.

Surface area measurement

Fig. 4 illustrates the N_2 adsorption–desorption study of the synthesized material. It shows type IV isotherm with H3 hysteresis loop which indicates the formation of slit-like pores with non-consistent size and/or shape.[19] The desorption data originated PSD curve (inset of Fig. 4) supports the observation about the nonexistence of regular shape and size of the pores in the sample. The BET surface area, total pore volume and pore diameter are found to be 41.7 m^2g^{-1}, 0.37 cm^3g^{-1} and 24.5 nm, respectively.

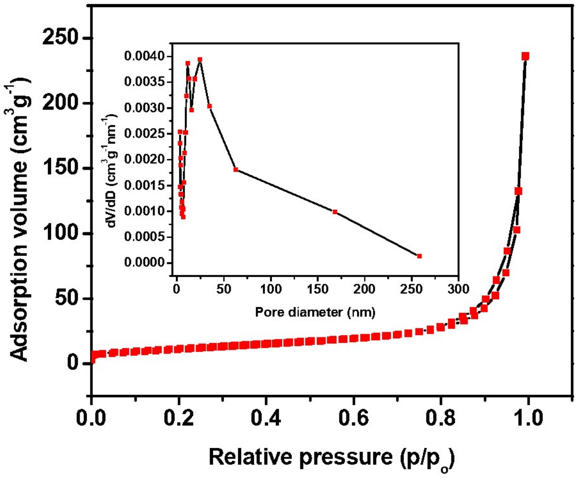
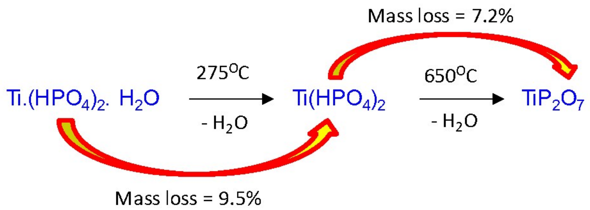


Figure 4. N_2 adsorption–desorption isotherm of the sample. Pore size distribution plot is shown in the inset.

TG analysis

The water content of the catalyst was verified by the TG analysis (Fig. 5), which indicates two steps mass loss as following.



About 9.5 % mass loss in the first step occurred due to the loss of crystalline water and the 7.2 % mass loss in the second step occurred due to the loss of lattice water. The total mass loss for the transformation of $Ti(HPO_4)_2.H_2O$ to TiP_2O_7 was found to be 16.7% which is comparable with theoretical mass loss, i.e, 14% for the above transformation. Therefore, we can conclude that the water is present in the synthesized sample.

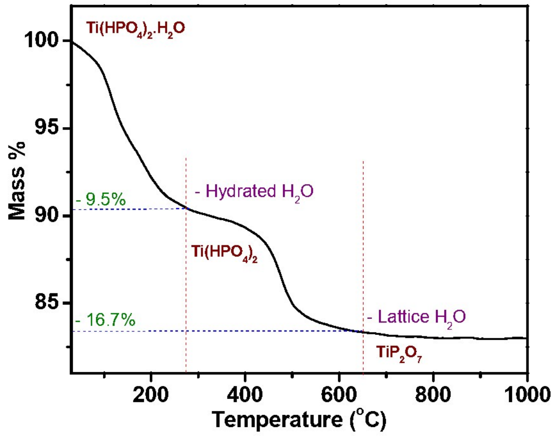


Figure 5. TG analysis of $Ti(HPO_4)_2.H_2O$ sample.

Microscopic Analysis

The FESEM image (Fig.6) indicates the hexagonal blocks are self-assembled together to form sheet-like structures. The same observation is established by the TEM image (Fig. 7a) of the sample, where the hexagonal blocks can be clearly noticed. The EDX plot (Fig. 7b) confirms the presence of O, Ti and P in the sample. The P : Ti atomic ratio is found to be 2.098 from the EDX plot, which indicates their uniform distribution in the sample. The TEM fringe of the material is shown in Fig. 7c which shows particular types of ordering.

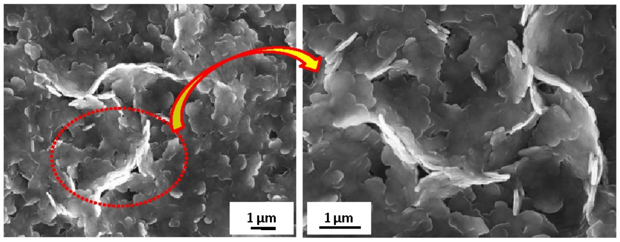


Figure 6. FE-SEM images of titanium phosphate.

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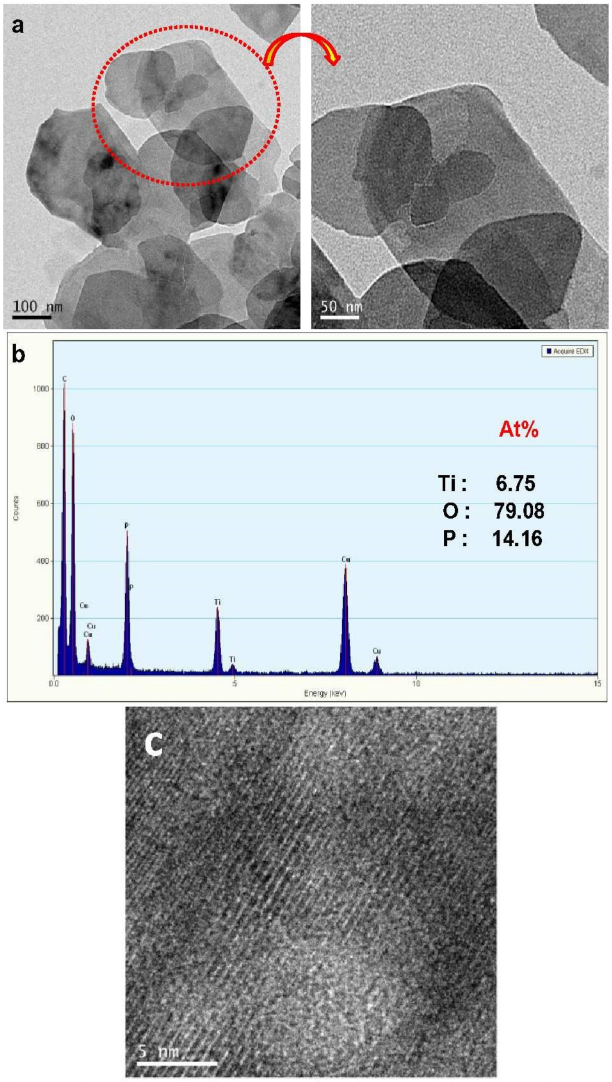
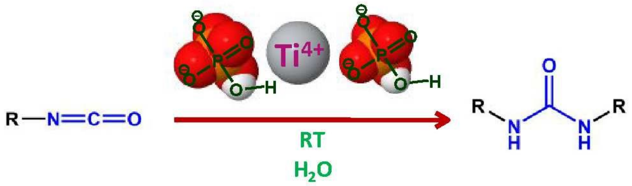


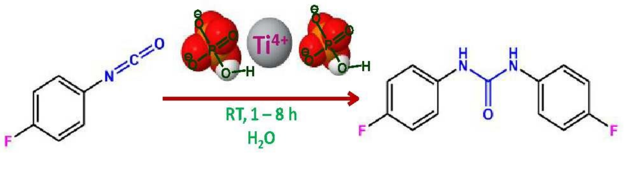
Figure 7. (a) TEM images, (b) EDX spectra and (c) TEM fringes of titanium phosphate.

Catalytic Activity

Green synthesis of urea catalyzed by mesoporous α $Ti(HPO_4)_2.H_2O$: The path of chemical transformation from isocyanate to urea is shown in scheme 1. The particular model urea synthesis was done using 5 mmol of 4-Fluorophenyl isocyanate as substrate (Scheme 2).



Scheme 1. General synthetic scheme of urea production.



Scheme 2. Synthetic scheme of urea production from 4-Fluoroplenyl isocyanate.

Although this method is not suitable for the preparation of urea derivatives, where the substituents of the two nitrogen atoms are different. As the reaction was done in very simplified and cost effective green condition, we only needed to optimize two major parameters of the reaction such as reaction time and catalyst loading. Figure 8 indicates that with increasing reaction time, product yield was also increased and moderate reaction yield (40%) was obtained only in 3 h of reaction time. 8 hours of reaction time was found to be the optimized time to carry out the reaction with product yield up to 93%. Figure 9 suggests that with increasing the amount of catalyst loading from 2 mg to 10 mg the urea product yield was increased from 29% to 93%. Further increase of catalyst loading did not affect the product yield. Therefore, the optimized quantity of catalyst loading was found to be 10 mg. Additionally, in absence of any catalyst there was no progress of the reaction was noticed.

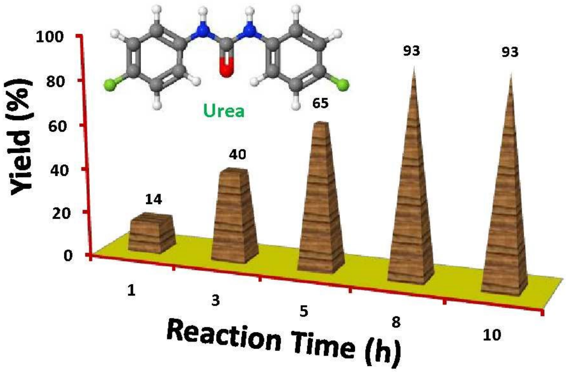


Fig. 8. Effect of reaction time on urea synthesis.

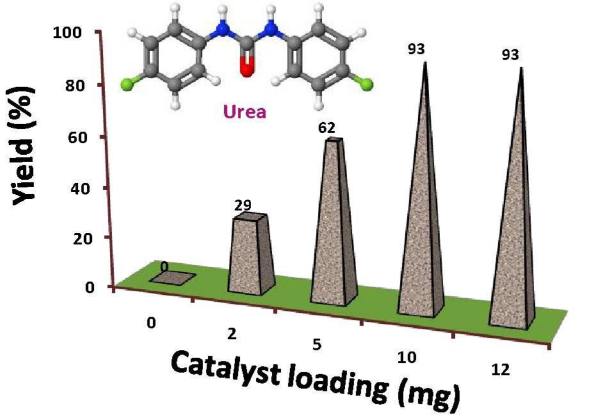


Fig. 9. Effect of catalyst loading on urea synthesis.

The catalytic activity of the titanium phosphate material was explored for urea synthesis from isocyanates with different kinds of isocyanate derivatives such as phenyl isocyanates with electron donating ($-CH_3$, $-OCH_3$) in addition to electron withdrawing (-Cl, -F) groups and naphthyl isocyanate (Table 1). It can be noticed from Table 1 that almost all the phenyl isocyanates produced the respective urea derivatives with excellent yields (Table 1, Entries 1-4) along with good TOF value upto 15.25 h^{-1}. Furthermore, the bulkier isocyanate, i.e., 1-Naphthyl isocyanate produced the corresponding urea derivative with comparatively poorer yield (72%) even after longer reaction time (10 h) (Table 1, Entry 5),

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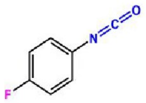
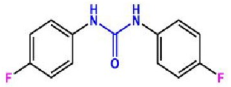
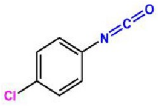
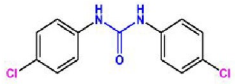
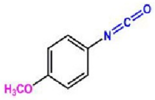
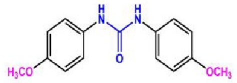
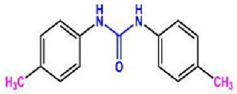
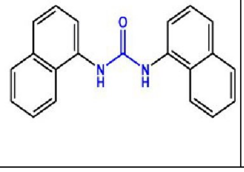
which may be due to decreased nucleophilicity because of the presence of an extra phenyl group.

Table 1. Ti(HPO_4)$_2$.H_2O catalyzed urea synthesis from various isocyanate derivatives.[a]

Entry	Isocyanate	Urea	Yield[b] (%)	TON/ TOF (h^{-1})
1			93	122 / 15.25
2			90	118 / 14.75
3[d]			91	120 / 15.00
4			92	121 / 15.13
5[c]			72	95 / 9.50

[a]Reaction conditions: 5 mmol isocyanate, H_2O (1mL), room temperature, catalyst: 10 mg, 8 h, [b]Isolated yield, [c]10h.

Proposed mechanism for urea synthesis

The predictable reaction mechanism for urea production from isocyanate utilizing α-Ti(HPO_4)$_2$·H_2O as the catalyst is revealed in Figure 10. The huge numbers of open active sites available on the 2-dimensional layered surface of the α-Ti(HPO_4)$_2$·H_2O surface decorated with consistent mesopores help to accelerate the catalysis reaction rate. The Ti^{4+} Lewis acidic sites of the catalyst trigger the isocyanate molecules.[17a] Then the activated isocyanate molecule undergoes C-N coupling with another isocyanate molecule and forms a four membered ring complex which is on reduction leads to the formation of urea derivative.[11] The ion-exchange property of Ti(HPO_4)$_2$·H_2O may promote the reduction reaction, whereas the catalyst regenerated similar ion exchanging with H_2O which is used as a solvent.[20]

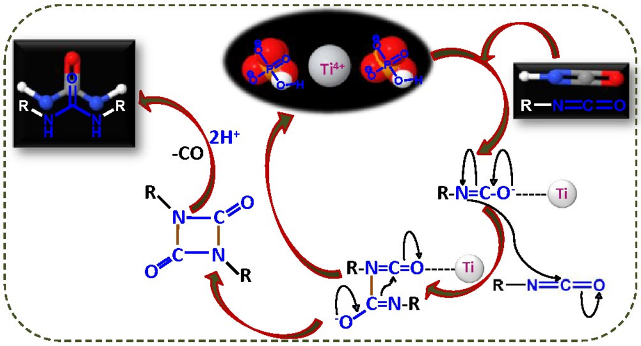
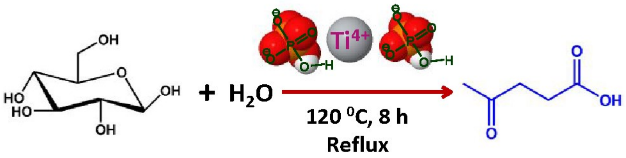


Figure 10. Probable mechanism for Ti(HPO_4)$_2$·H_2O catalysed urea synthesis from isocyanate.

LA synthesis catalyzed by mesoporous Ti(HPO_4)$_2$.H_2O:

The path of chemical transformation from glucose to LA is shown in scheme. 3.



Scheme 3. Synthetic scheme of LA production.

The reaction was standardized by varying different significant parameters such as catalyst loading and reaction temperature. The reaction was performed with increasing the amount of catalyst loading from 10 mg to 30 mg or more for 8 h (Figure 11), the isolated LA product yield was increased from 23% to 80%. Therefore, the optimized amount of catalyst loading was found to be 30 mg. It is important to notice that in absence of any catalyst there was no progress of the reaction was noticed. Therefore, the synthesized mesoporous Ti(HPO_4)$_2$.H_2O successfully increased the reaction rate like an efficient catalyst, which may be due to the open active acidic sites present in the 2D hexagonal blocks of the catalyst material.[13] Furthermore, performing the reaction at room temperature (30 ^{0}C), only trace amount of LA product was obtained (Figure 12). Figure 5 illustrates that the glucose to LA conversion reaction is temperature dependent. With increasing temperature, LA yield also increases. The glucose to LA conversion was increased 6 fold with increasing temperature from room temperature to 60 ^{0}C. We have obtained 80% of LA yield at 120 ^{0}C reaction temperature. Further increase of temperature did not affect significantly the amount of product yield. Therefore, the optimized reaction temperature was found to be 120 ^{0}C.

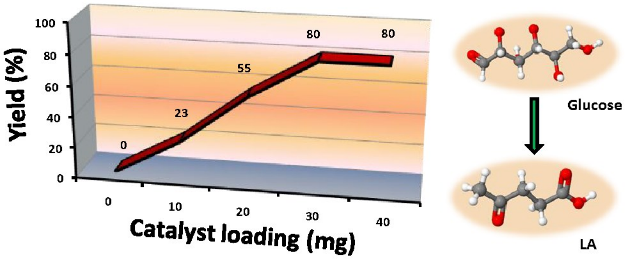


Figure 11. Effect of catalyst loading on glucose to LA conversion.

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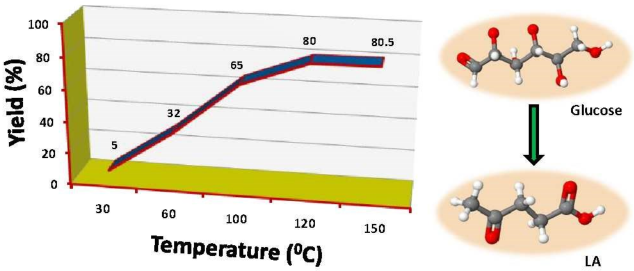
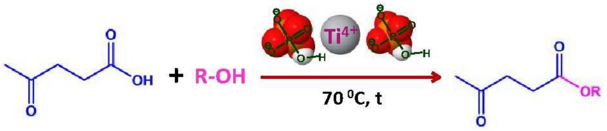


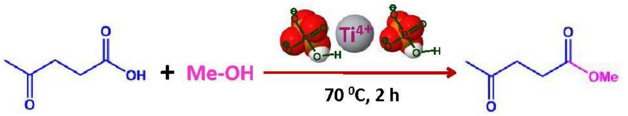
Figure 12. Effect of reaction temperature on glucose to LA conversion.

Esterification of LA using alcohols catalyzed by mesoporous $Ti(HPO_4)_2.H_2O$:

The path of chemical transformation from LA to levulinate esters is shown in scheme. 4. The particular model esterification reaction was done in presence of MeOH (Scheme 5).



Scheme 4. Synthetic scheme of levulinate ester production.



Scheme 5. Synthetic scheme of leuvlinate ester production with methanol.

The reaction was optimized by varying different significant parameters such as solvent amount, reaction time and catalyst loading. Table 2 indicated that with increasing solvent amount product yield was also improved (Table 2, entries 1 - 4) and 3 mL of solvent was found to be the optimized amount of solvent to carry out the reaction (Table 2, entry 4). It can be noticed from Table 2 that the rate of the reaction is very fast and moderate amount of yield (43%) was observed within only first 30 minutes of the esterification reaction (Table 2, entry 7). Table 2 also indicated that with increasing reaction time product yield was also improved (Table 2, entries 4 - 7) and 2 hours of reaction time was found to be the optimized reaction time to carry out the reaction (Table 2, entry 4). When the reaction was carried out at room temperature only 52% yield of the methyl levulinate product was observed after 2 hours (Table 2, entry 8).

Figure 13 suggested that with increasing the amount of catalyst loading from 5 mg to 15 mg or more, the methyl levulinate product yield was increased from 35% to 99%. Therefore, the optimized amount of catalyst loading was found to be 15 mg. Additionally, in absence of any catalyst insignificant amount of product was obtained.

Table 2. Effect of solvent amount and reaction time on LA conversion to methyl levulinate [a].

Entry	Solvent amount (ml)	Reaction time (min)	Yield (%)[b]
1	0.5	120	45
2	1	120	67
3	2	120	80
4	**3**	**120**	**99**
5	3	90	87
6	3	60	65
7	3	30	43
8[c]	3	120	52

[a] Reaction conditions: 5 mmol LA, alcohol, temperature: 70 0C, catalyst: 15 mg, [b] GC yield, [c] at r.t.

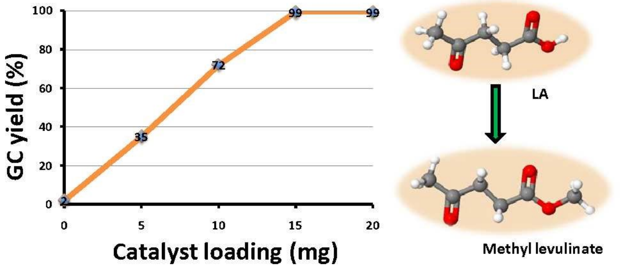
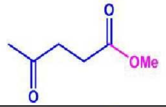
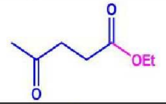
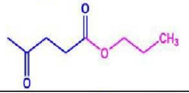
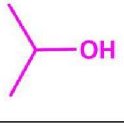
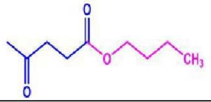


Fig. 13. Effect of catalyst loading on LA conversion.

The catalytic activity of the titanium phosphate material was explored for LA esterification reaction with different kinds of alcohols (methanol, ethanol, n-propanol, iso-propanol and n-butanol) (Table 3). It can be noticed from Table 3 that almost all the alkyl levulinate products showed excellent yields with excellent selectivity (>99%) for all the desired products. It is important to notice that alcohols with bulkier groups (entries 3 - 5) showed a little lower yield of the respective levulinate products that that of methanol or ethanol (entries 1, 2).

Table 3. LA conversion using various alcohols over titanium phosphate nanomaterial[a]

Entry	Solvents	Products	Isolated Yield (%) [Selectivity (%)]	TON/ TOF (h^{-1})
1	MeOH		98 [>99]	86 / 43.0
2	EtOH		98 [>99]	86 / 43.0
3			94 [>99]	83 / 41.5
4			93 [>99]	82 / 41.0
5			90 [>99]	79 / 39.5

[a] Reaction conditions: 5 mmol LA, 3 mL alcohol, temperature: 70 0C, catalyst: 15 mg, reaction time: 2 h.

Proposed mechanism for esterification of LA

The predictable reaction mechanism[21] for LA esterification with alcohol utilizing α-$Ti(HPO_4)_2{\cdot}H_2O$ as the catalyst is revealed in Figure 14. There are several Brønsted acid sites available on the surface of the 2-dimensional layered α-$Ti(HPO_4)_2{\cdot}H_2O$[22]. The LA molecule is adsorbed on the adsorb Brønsted acid site resulting protonated LA intermediate. The nucleophilic oxygen atom of alcohol molecule then attacks the highly electrophilic carbonyl carbon of the intermediate forming an oxonium ion which leads to the formation of levulinate ester along with regeneration of catalyst through three consecutive steps: proton transfer, dehydration and deprotonation respectively.

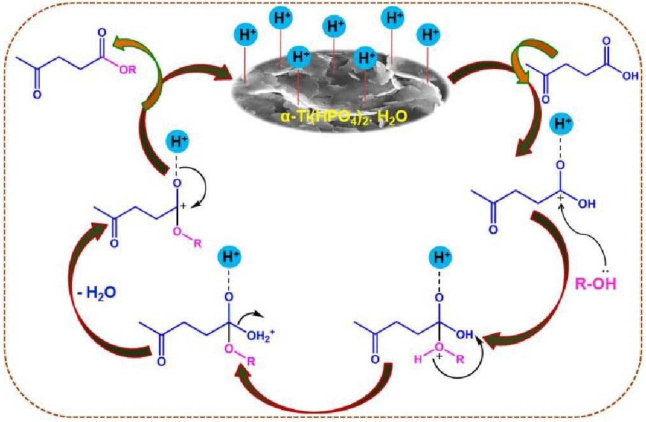


Figure 14. Probable mechanism for $Ti(HPO_4)_2{\cdot}H_2O$ catalysed esterification of LA with alcohol.

Recyclability of titanium phosphate material

The titanium phosphate material was collected from the reaction mixture after closing the reaction *via* centrifugation. Then the recovered catalyst was washed with water followed by acetone for 2-3 times and dried in oven at 60 ^{0}C for 2 hours. After that the recovered catalyst was reused for five cycles for urea synthesis, LA synthesis and LA to levulinate ester production reactions under standardized conditions (Figure 15). The catalyst showed minimal decrease in the desired product yields for all the reactions after five reaction cycles. After completion of the fifth cycle the yields of the desired products dropped down to 82%, 72%, 89% for urea synthesis, LA synthesis and LA to levulinate ester production, respectively. This deactivation may be caused by blocking of the pores of the mesoporous catalyst material by the intermediate products and the final products.[21] Further microscopic study (FESEM and TEM) of the recycled catalyst (Figure 16) revealed that the α-$Ti(HPO_4)_2$. H_2O material retained its morphology and internal structure after catalytic runs.

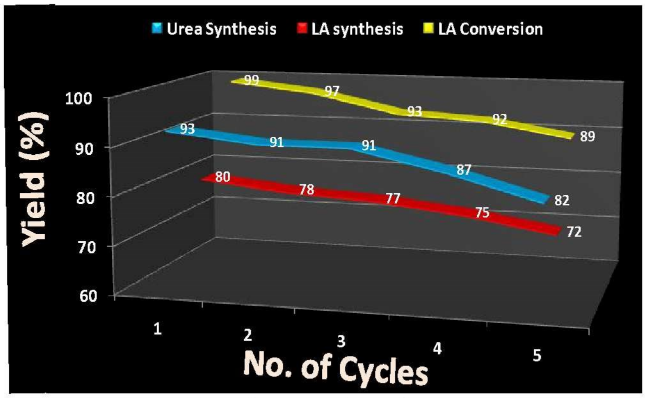


Figure 15. Recyclability diagram of titanium phosphate catalyst under standardized reaction condition.

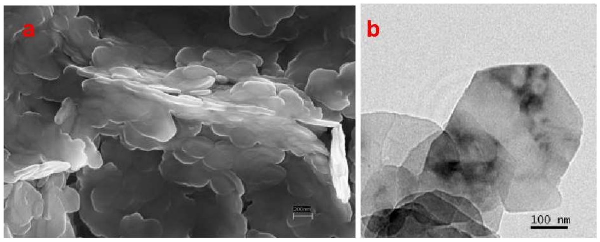


Fig. 16. (a) FEMEM and (b) TEM images of the recycled catalyst.

The relative study (Table 4) between our catalytic systems with formerly reported systems reveals that the present system provides some advantages for the reported reactions, such as all the reactions are performed in green and facile catalytic conditions without using any hazardous solvents. The reaction set-ups of the present studies are also very simple and cost-effective, as well as all the reactions are end up with better yield of the respective products. Therefore, the synthesized mesoporous $Ti(HPO_4)_2.H_2O$ material is found to be a cheap, reusable and efficient heterogeneous catalyst for urea synthesis from isocyanates, glucose to LA and LA to levulinate ester conversion reactions.

Table 4. Comparative chart of the present catalytic system with other reported systems.

Reaction	Catalyst	Reaction condition	Yield (%)	References
Urea Synthesis	$[C_{52}H_{58}CoN_2O_2]$; $[CoL^{AP(Ph)}L^{ISQ(Ph)}]$	Phenyl isocyanate, 5 mL Dry DCM, Ar pressure tube, 36 ^{0}C temperature, Sunlight, catalyst: 2.5 mol%, reaction time: 6 h	86	11
	Titanium phosphate nanomaterial	**5 mmol 4-Fluorophenyl isocyanate, 1 mL H_2O, room temperature, catalyst: 10 mg, reaction time: 8 h**	**93**	**This study**
LA Synthesis	ZrHyC	100 mg glucose, 6 mL solvent (5 mL THF + 1 mL H_2O), microwave reactor, temperature: 65 ^{0}C, catalyst: 20 mg, reaction time: 20 min.	67	23

DOI: 10.1039/D0NJ03182H

LA Esteri-fication	**Titanium phosphate nanomaterial**	**100 mg glucose, 10 mL H_2O, temperature: 120 ^0C, catalyst: 30 mg, reaction time: 8 h.**	**80**	**This study**
	20 wt% $H_4SiW_{12}O_{40}$-SiO_2	catalyst (104 mg), LA (205 mg), ethanol (2 mL) cyclohexane (5 mL), 75 °C, 6 h.	75	24

Conclusions

At last, we can conclude that in the present study, a mesoporous sheet-like 2D α-$Ti(HPO_4)_2$. H_2O nanomaterial is synthesized through a facile solvothermal method. The material holds ordered mesopores throughout its hexagonal building blocks as well as 3.86 eV band gap energy. The synthesized titanium phosphate nanomaterial shows brilliant catalytic conversion efficiency for the selective synthesis of ureas from a broad range of isocyanates in presence of H_2O at room temperature with high product yield (up to 93%) and TOF value up to 15.25 h^{-1}. Optimization study reveals that the production of urea depends on several parameters like reaction time, catalyst loading, bulkiness or nucleophilicity of isocyanate substrate etc. Bulkier isocyanate (1-Naphthyl isocyanate) is observed to produce the corresponding urea derivative with comparatively poorer yield with a slower reaction rate than that of phenyl isocyanates. The α-$Ti(HPO_4)_2$. H_2O nanomaterial also catalytically converts glucose levulinic acid (LA) and subsequently LA to alkyl levulinates in presence of different alcohols with high product yield (up to 98%) and TOF value 43.00 h^{-1}. Moreover, the α-$Ti(HPO_4)_2$. H_2O catalyst is also found to be reusable for multiple cycles of all the reactions keeping its catalytic efficiency along with its structural and morphological characteristics unaltered.

Acknowledgements

SMI is thankful to the DST-SERB and BRNS, Govt. Of India for financial support. AHC is thankful to University of Kalyani, India for providing her URS fellowship. I.H.C. is thankful to CSIR, India (09/106 (0181) 2019 EMR-I) for her fellowship. PC is thankful to the Govt. of West Bengal for her SVMCM fellowship.

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View Article Online
DOI: 10.1039/D0NJ03182H

Graphical Abstract

Catalytic Conversions of Isocyanate to Urea and Glucose to Levulinate Esters over Mesoporous α-Ti(HPO_4)$_2$. H_2O in Green Media

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