


 Cite this: *RSC Adv.*, 2017, **7**, 25589

 Received 14th March 2017
 Accepted 5th May 2017

 DOI: 10.1039/c7ra03051g
rsc.li/rsc-advances

Highly active $\text{g-C}_3\text{N}_4$ as a solid base catalyst for Knoevenagel condensation reaction under phase transfer conditions†

 Priti Sharma * and Yoel Sasson

In a promising approach, heterogeneous $\text{g-C}_3\text{N}_4$ as a solid base catalyst exhibits appreciable activity in Knoevenagel condensations at room temperature for the synthesis of substituted stilbene in presence of a crown-ether phase transfer catalyst. High yield of the product substituted stilbene were isolated in a very short reaction time period (~30 min). The solid base $\text{g-C}_3\text{N}_4$ catalyst was proven to be recyclable for several runs. Various aromatic substrates were screened using heterogeneous base $\text{g-C}_3\text{N}_4$ catalyst, exhibiting appreciable corresponding product yield (~99%) at room temperature.

Introduction

The base catalyzed organic reactions are of great importance in the chemical process industry. Typical examples are aldol condensations, Knoevenagel condensations and transesterification reactions.^{1–4} However, the above mentioned name reactions typically require stoichiometric amounts of base along with several reaction conditions such as high reaction temperature, long reaction time and lack of recyclability.⁵ Over the decades researchers have sought solid base catalysts such as metal oxides^{6–8} organic materials⁹ or alkali doped mesoporous,¹⁰ zeolites¹¹ or other solid supported materials.^{12,13} Nevertheless such materials are often unstable, and suffer from leaching and deactivation partial decomposition under harsh reaction condition and low turnover numbers are obtained.¹⁴ Recently organocatalysis has emerged as a promising technology for application in green catalysis applications.^{15–17} In the same context, $\text{g-C}_3\text{N}_4$, metal free organocatalyst semiconductors was recently reported as an efficient and environmentally benign photo catalyst with working capacity under visible light.^{18–22} However, the surface basic nature of $\text{g-C}_3\text{N}_4$ is relatively less explored in organocatalysis application.²³ The fabrication of $\text{g-C}_3\text{N}_4$ is based on direct thermal condensation of high nitrogen content precursor example, urea, cyanamide or dicyandiamide.²⁴ Consequently, $\text{g-C}_3\text{N}_4$ opens the doors of Lewis-base characters for coordination chemistry and base-catalyzed organic reactions.²⁵ In a notable work Vinu *et al.*

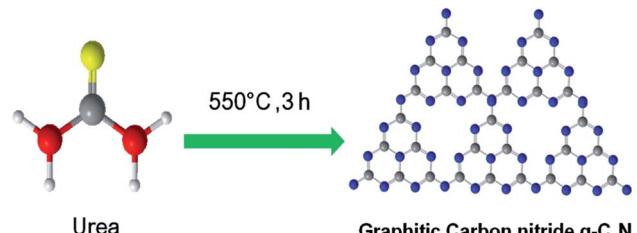
claims synthesis of $\text{g-C}_3\text{N}_4$ carbon nitride mesoporous nanoparticles with high nitrogen content, exhibited appreciable catalytic transesterification of β -keto esters with different alcohols at temperature of 110 °C.²⁶ In another work Bitter *et al.* reported basic nitrogen containing carbon nanotubes synthesis (various amount of pyridine nitrogen incorporation) and its catalytic activity in Knoevenagel condensations at 80 °C.²⁷ Recently, Park and coworkers demonstrated mesoporous carbon nitride (MCN) as base catalyst for Knoevenagel condensation of aromatic aldehydes with ethylcyanoacetate by using microwave irradiation.²⁸

In addition W. Fan *et al.* described the controlled synthesis of $\text{g-C}_3\text{N}_4$ with high nitrogen content (modified) and claims higher product yield (40 °C).²⁹ Further, in a remarkable series of work Markus Antonietti exhibited the lewis base character of mpg– C_3N_4 in the various applications *viz.*; aliphatic C–H bond oxidation,³⁰ aerobic oxidative coupling of amines,³¹ selective oxidation of alcohols using visible light.³² Recently Markus Antonietti, extend the application of deprotonated (treated with aq. tBuOK, KOH or K_2CO_3) mesoporous graphitic carbon nitride (mpg– C_3N_4) catalysts screened for Knoevenagel and transesterification reactions at 110 °C.³³ However, the reported procedure for Knoevenagel condensation reaction faces the drawback of high temperature, long reaction time period and most of these catalysts are not completely recyclable. In addition the above fabrication methods are not efficient and not suitable for large scale applications. Stilbenes and its derivatives are important intermediates in the agrochemical^{34–36} polymer,^{37,38} food³⁹ pharmaceutical industries^{40–42} Moreover stilbene synthesis reported procedures suffer from long reaction time, high metal content, high base usage, non recyclable and accidental prone at higher temperature.^{43,44–46} On the other hand phase transfer catalysis (PTC) offer, efficient, mild and environment friendly reaction conditions, with the replacement of hazardous and sensitive bases or other chemicals.^{47–52}

Casali Center of Applied Chemistry, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel. E-mail: priti.sharma@mail.huji.ac.il

† Electronic supplementary information (ESI) available: Physical appearance of $\text{g-C}_3\text{N}_4$, SEM-EDX images $\text{g-C}_3\text{N}_4$, TEM-EDX images $\text{g-C}_3\text{N}_4$, TEM images of $\text{g-C}_3\text{N}_4$ with different magnification & SAED pattern, characterization, experimental, heterogeneous study of catalyst $\text{g-C}_3\text{N}_4$. See DOI: [10.1039/c7ra03051g](https://doi.org/10.1039/c7ra03051g)



Scheme 1 $g\text{-C}_3\text{N}_4$ synthesis from urea.

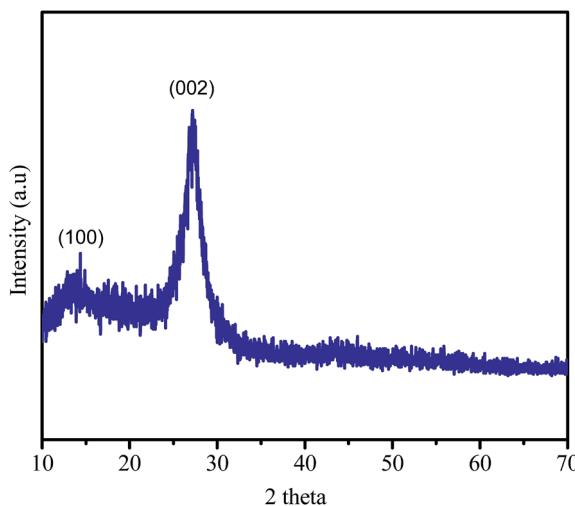
In the present research study we combined the solid base $g\text{-C}_3\text{N}_4$ with a phase transfer agent to catalyze the Knovenagel condensation under ambient conditions, to the best of our knowledge this combination is novel and was not reported previously. We have examined various governing factors such as, various phase transfer catalysts (PTC), solvent, temperature effect and different substrates. The optimized procedure yielded over 90% yield of several stilbene derivatives (Scheme 1).

Results and discussion

Solid basic $g\text{-C}_3\text{N}_4$ catalyst is formulated *via* using urea and following the known reported procedure by Wei Chen *et al.*⁵³ The obtained solid in pale yellow color $g\text{-C}_3\text{N}_4$ was thoroughly analyzed by physicochemical characterization techniques (Scheme 1) (Fig. S1–S8†).

The typical X-ray diffraction (XRD) pattern of $g\text{-C}_3\text{N}_4$ material is depicted in Fig. 1. The formation of $g\text{-C}_3\text{N}_4$ is clearly observed in the XRD pattern where after calcination at 550 °C for 3 h, intense typical peaks at 13.20° and 27.20° appeared (Fig. 1). These peaks are in good agreement with reported values which attributes to (100) and (002) diffraction plane, respectively (Fig. 1).⁵⁴ The intense XRD peak of solid basic $g\text{-C}_3\text{N}_4$ at 27.2° corresponds to the (002) plane and is characteristic for stacking of the conjugated aromatic system (Fig. 1).⁵⁵

Fabrication of $g\text{-C}_3\text{N}_4$ from urea is well characterized also by FTIR spectroscopy and visualized in Fig S2† (a) urea, (b) $g\text{-C}_3\text{N}_4$.

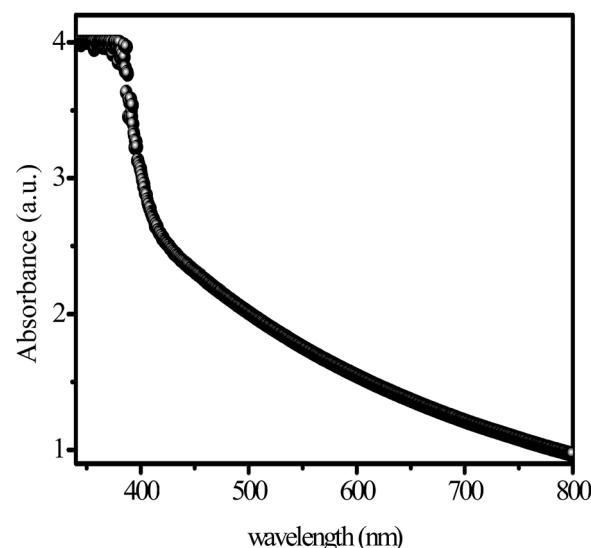
Fig. 1 XRD pattern of $g\text{-C}_3\text{N}_4$.

The characteristics absorption bands of urea (1456, 1578, 3435, 3341 cm^{-1}) were disappeared after transformation into solid basic $g\text{-C}_3\text{N}_4$ *via* controlled calcinations (urea at 550 °C for 3 h) (Fig. S2a and b†). Additionally, the characteristic breathing mode of the triazine repeating units at 810 cm^{-1} , related to the *s*-triazine ring absorption band vibrations; which are well observed in synthesized $g\text{-C}_3\text{N}_4$ pale yellow material (Fig. S2b†). The strong intense bands at 1625, 1550, 1410 and 1250 cm^{-1} were in good agreement to the reported values of typical stretching vibration modes of triazine derived repeating units (Fig. S2b†).⁵⁶

The optical properties of synthesized material, solid basic $g\text{-C}_3\text{N}_4$ were analyzed by UV-vis spectroscopy. Synthesized solid basic $g\text{-C}_3\text{N}_4$ show maximum absorption below 550 nm (visible range), which attributes valence band (VB) to the conduction band (CB) transition (Fig. 2).⁵⁷

A detail XPS study was carried out for molecular arrangement with chemical properties with systematic formation analysis of heterogeneous basic $g\text{-C}_3\text{N}_4$ catalyst, (Fig. S3A–C†). In the displayed C1s spectrum shows two characteristic peaks corresponding the (−C−N−) and (−N=C−) at 284.8 and 288 eV; respectively in the fabricated $g\text{-C}_3\text{N}_4$ material (Fig. S3C†). High resolution N1s spectrum of $g\text{-C}_3\text{N}_4$ the N1s spectrum clearly deconvoluted into three intense peaks at 399.9, 401.3 and 405.6 eV, respectively (Fig. S3B†). The peak at 399.9 eV is assigned to the presence of pyridine-*N* species [sp^2 -hybridized nitrogen (C=N−C)], where each nitrogen (N) atom is bonded to two carbon atoms within aromatic ring located at edges of the graphite planes of $g\text{-C}_3\text{N}_4$ material (Fig. S3B†). The peak at 401.3 eV corresponds to nitrogen atoms trigonally bonded with C carbon (sp^2 or sp^3) atoms of amino functional groups (C−N−H). Whereas, the peak at 405.6 eV describes the terminal amino groups (−NH₂), which is considered to be strong reason for the enhancing basic nature to the solid $g\text{-C}_3\text{N}_4$ material (Fig. S3B†).

The morphologies of $g\text{-C}_3\text{N}_4$ material visualized by SEM spectroscopy with different magnification at 5 μm , 2 μm and 1

Fig. 2 $g\text{-C}_3\text{N}_4$ UV-vis spectra.

μm respectively (Fig. 3A–C). The monomer unit of g-C₃N₄ appeared to aggregation of uniform sheet structure, each particle agglomeration of many small layers in g-C₃N₄.⁵⁸ Moreover, the EDX pattern of g-C₃N₄ indicates the presence of elementary carbon and nitrogen in the synthesized solid basic g-C₃N₄ material (Fig. S5†). The morphological representative TEM images of g-C₃N₄ material at 1 μm, 100 nm and 10 nm scale show crumpled sheets, multilayer with a graphite like structure (Fig. 4A–C).^{57,59} Furthermore, the SAED pattern shows a broad ring with lower intensity, supports amorphous nature of the synthesized g-C₃N₄ heterogeneous basic materials (Fig. S6 and S7†).

The surface textural properties of the synthesized samples are determined with the help of the BET multilayer adsorption

and desorption analysis. The calculated BET surface area is 15.00 m² g⁻¹, total pore volume (V_p) 0.013 cm³ g⁻¹, and mean pore size (radius) D_v(r) of g-C₃N₄ is found to be 15.3 nm, respectively (Fig. S4†).⁵⁶

A classical Knoevenagel condensation reaction, proceeds with stoichiometric amount of base at higher temperature with standard substrates.^{60,61} Here we tried to develop a protocol under mild reaction condition (precisely at room temperature and short reaction time period) using phase transfer catalyst (PTC) with heterogeneous g-C₃N₄ base in nature catalyst to activate the substrate at room temperature and with minimum time period to afford the appreciable corresponding yield selectively.

In the present study, we exclusively used g-C₃N₄ basic in nature as the heterogeneous catalyst with phase transfer catalyst for the Knoevenagel condensation reaction (Schemes 2 and 3). For the efficiency measurement of g-C₃N₄ with phase transfer catalyst a model reaction was chosen between 4-nitrotoluene (1 mmol), benzaldehyde (1 mmol), at room temperature (25 °C) with 18Crown ether 6 (0.1 mmol) (PTC), solvent toluene (5 mL), g-C₃N₄ catalyst (30 mg) (Schemes 2 and 3). Within a short reaction time period (30 min) the product formation of 4-nitro *trans*-stilbene is confirmed with GC in excellent yield (99%). Interestingly, Knoevenagel condensation reaction progresses smoothly in presence of basic g-C₃N₄ heterogeneous catalyst with PTC in a quite short reaction time period (30 min) at room temperature (25 °C) to afford the corresponding product yield.

The Knoevenagel reaction has been studied for solvent impact using different solvents namely the highly polar DMSO, DMF and non-polar toluene. Reaction was carried out in highly polar solvent with DMSO and DMF as solvent under optimized reaction condition [4-nitrotoluene (1 mmol), benzaldehyde (1 mmol), room temperature (25 °C), 18Crown ether 6 (0.1 mmol) (PTC), solvent (5 mL), catalyst g-C₃N₄ (30 mg)] resulting in 10% and 15% yield of corresponding product respectively in 5 h of reaction time period. Surprisingly with non polar solvent toluene with g-C₃N₄ basic heterogeneous catalyst reaction progress selectively to yield 4-nitrostilbene product with 99% yield under same optimized reaction conditions within 30 min

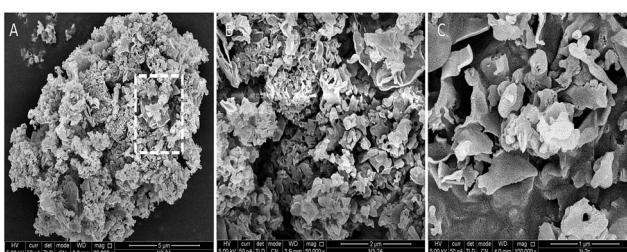


Fig. 3 SEM images of g-C₃N₄ at different magnifications: (A) at 5 μm g-C₃N₄, (B) at 2 μm g-C₃N₄, (C) at 1 μm g-C₃N₄.

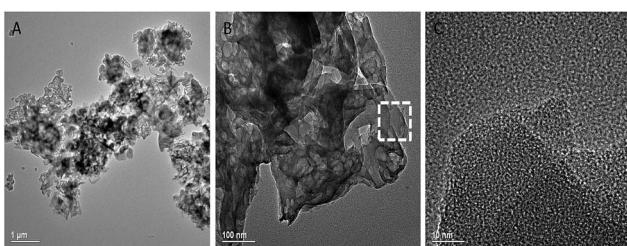
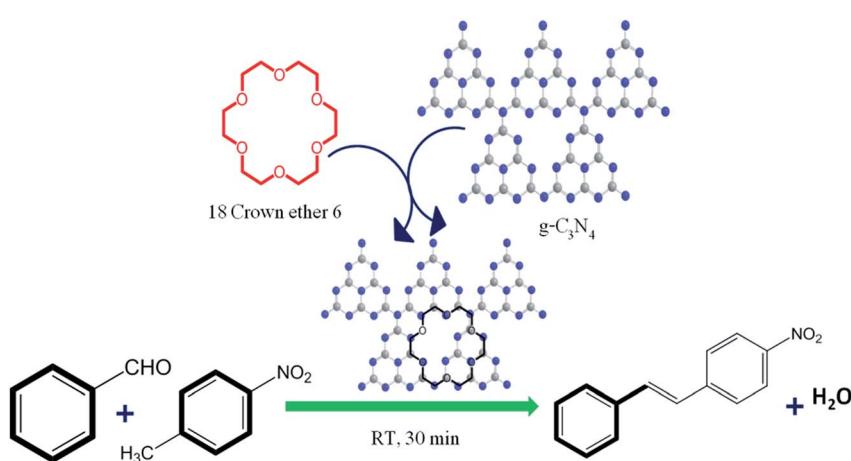
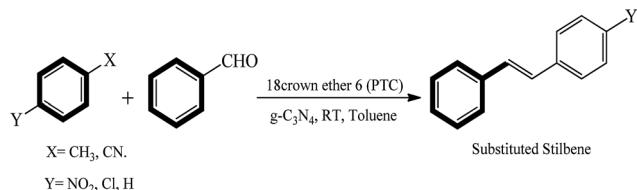


Fig. 4 TEM images of g-C₃N₄ at different magnifications: (A) at 1 μm g-C₃N₄, (B) at 100 nm g-C₃N₄, (C) at 10 nm g-C₃N₄.



Scheme 2 g-C₃N₄ catalyzed Knoevenagel condensation with 18Crown ether using benzaldehyde and 4-nitrotoluene.



Scheme 3 Knoevenagel condensation reaction using $g\text{-C}_3\text{N}_4$ with PTC at room temperature.

of reaction time period. This might be due to nonpolar solvent toluene might have easily provided the accessibility of 18Crown ether 6 (PTC) to $g\text{-C}_3\text{N}_4$ due to nonpolar nature. Therefore, toluene as solvent is chosen for the rest of the reaction optimization procedures. However without 18Crown ether 6 (PTC) no product formation was detected under optimized reaction condition with toluene solvent even after 5 h.

In the present study, for the establishment the role of phase transfer catalyst we proceeded with model reaction between 4-nitrotoluene (1 mmol), benzaldehyde (1 mmol), at room temperature (25 °C) with PTC (0.1 mmol), solvent toluene (5 mL) and $g\text{-C}_3\text{N}_4$ catalyst (30 mg). We screened the several phase transfer catalysts under optimized reaction conditions, *viz.*; TBAB (tetrabutyl ammonium bromide), THAB (tetrahexyl ammonium bromide), THAB (tetrabutyl ammonium iodide), THAB (tetrahexyl ammonium chloride), THAB (tetraethyl ammonium chloride) and 18Crown ether 6. The screened results were summarized in Table 1. From Table 1 result describe itself clearly among all the screened phase transfer catalysts only 18Crown ether 6 (PTC) is surprisingly working at room temperature (25 °C) and affords 99% yield of corresponding product within a short reaction time period (1 h) (Table 1 entry 6). The appreciable reactivity of 18Crown ether 6 (PTC) is might be due to the cyclic structure owning highly flexible, good binding affinity, and selective, which is more appropriate to access the $g\text{-C}_3\text{N}_4$ active site, rather than long aliphatic chain of other phase transfer catalysts (Table 1 entries 1–6). Further, Glyme^{62,63} (open-chain analogues of crown ethers) *viz.*; diglyme [bis(2-methoxyethyl)ether], triglyme [1,2-bis(2-

methoxyethoxy)ethane were tested as PTC for the Knoevenagel reaction under optimized reaction conditions with standard reactants. The obtained results exhibited ~10% conversion of substituted *E*-stilbene. From Table 1 clears the open chain crown ethers are not much efficient to initiate the reaction in comparison to closed chain crown ether as PTC (Table 1 entries 7, 8).

To designate the basic role of $g\text{-C}_3\text{N}_4$ heterogeneous catalyst in a Knoevenagel condensation reaction under optimized reaction *via* model reaction using 4-nitrotoluene (1 mmol) and benzaldehyde (1 mmol), at room temperature (25 °C) with PTC (0.1 mmol), solvent toluene (5 mL) and $g\text{-C}_3\text{N}_4$ (30 mg) catalyst is performed. For the reaction progress crosscheck, samples were withdrawn periodically (15 min) from the reaction mixture and analyzed by GC. In a controlled experiment without $g\text{-C}_3\text{N}_4$ catalyst reaction is performed under optimized reaction condition (Table 2, entry 1). The result of controlled experiment shows no progress of reaction in absence of $g\text{-C}_3\text{N}_4$ catalyst. Further, another set of controlled experiments were performed at higher temperature (at 50 °C, 60 °C, 70 °C) without the use of $g\text{-C}_3\text{N}_4$ using model reaction substrates. The result do not shows any appreciable progress of reaction (10%). The result signifies that only higher temperature is not sufficient to initiate reaction, base usage also plays a crucial role in Knoevenagel condensation reaction (Table 2, entry 2).

A new set of reaction with inorganic base (KOH, K_2CO_3) were screened under optimized reaction condition 4-nitrotoluene (1 mmol) and benzaldehyde (1 mmol), at room temperature (25 °C) with 18Crown ether 6 (PTC) (0.1 mmol) and solvent toluene (5 mL). M. Chidambaram *et al.* reported⁶⁴ inorganic base KOH and K_2CO_3 reactivity with 18Crown ether 6 (PTC), shows 98% yield at room temperature, which we also reproduced with 99% conversion of corresponding product (Table 2, entry 3, 4). But unfortunately this procedure (use of KOH and K_2CO_3) does not provide the recyclability of base which is essential criteria for environment friendly and industrial process for continuous production.

From all the conducted experiments it is clear that a combination of heterogeneous basic catalyst $g\text{-C}_3\text{N}_4$, with 18Crown

Table 1 Phase transfer catalysts screening for Knoevenagel condensation reaction^a

Entry	PTC	Time (h)	Yield (%)
1	Tetrabutyl ammonium bromide (TBAB)	12	10
2	Tetrahexyl ammonium bromide (THAB)	12	~2
3	Tetrabutyl ammonium iodide (THAB)	12	~5
4	Tetrahexyl ammonium chloride (THAB)	12	~2
5	Tetraethyl ammonium chloride (THAB)	12	~1
6	18Crown ether 6	30 min	99%
7#	Diglyme [bis(2-methoxyethyl)ether]	12	10
8#	Triglyme [1,2-bis(2-methoxyethoxy)ethane]	12	10

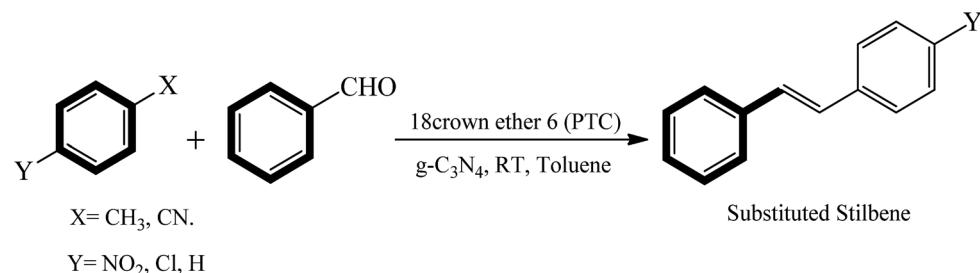
^a Reaction conditions: 4-nitrotoluene (1 mmol), benzaldehyde (1 mmol), room temperature (25 °C), PTC (0.1 mmol), solvent toluene (5 mL) and $g\text{-C}_3\text{N}_4$ catalyst (30 mg). # glyme (3 mL).

Table 2 Knoevenagel condensation reaction optimization under various parameters^a

Entry	Reaction parameter	Time (h)	Yield (%)
1	18Crown ether 6 (PTC)	12	5
2	18Crown ether 6 (PTC) + heat (50 °C, 60 °C, 70 °C)	12	5, 10, 10
3	18Crown ether 6 (PTC) + KOH	1	99
4	18Crown ether 6 (PTC) + K_2CO_3	1	98
5	$g\text{-C}_3\text{N}_4$	12	~1
6	$g\text{-C}_3\text{N}_4$ + heat	12	88
7	18Crown ether 6 (PTC) + $g\text{-C}_3\text{N}_4$	30 (min)	99
8	(Blank reaction)	12	00

^a Reaction conditions: 4-nitrotoluene (1 mmol) and benzaldehyde (1 mmol), at with PTC (0.1 mmol), solvent toluene (5 mL), base & $g\text{-C}_3\text{N}_4$ catalyst (30 mg).



Table 3 Screening of $\text{g-C}_3\text{N}_4$ catalyst using PTC for Knoevenagel condensation with different substrates^a

Entry	Substrate 1	Substrate 2	Product	Time (min)	Yield (%)
1				30	99
2				30	99
3				30	99
4				30	99
5				30	85
6				30	88
7				30	80
8				30	85

^a Reaction conditions: substrate 1 (1 mmol) and substrate 2 (1 mmol), at room temperature (25 °C), 18Crown ether 6 (PTC) (0.1 mmol), solvent toluene (5 mL) and $\text{g-C}_3\text{N}_4$ basic catalyst (30 mg).

ether 6 (PTC) at room temperature (25 °C) is necessary to improve towards more economic Knoevenagel condensation rather than classical condensation reaction (Table 2). The performed reaction establishes a peculiar role of phase transfer catalyst for Knoevenagel condensation reaction at room temperature (Tables 1 and 2).

After optimizing the reaction protocol for Knoevenagel condensation model reaction and interesting exclusive results within a short reaction time period, we proceeded to screen the $\text{g-C}_3\text{N}_4$ heterogeneous basic catalyst with 18Crown ether 6 (PTC) combinations with different substrates. Various reactants were analyzed and results are summarized in Table 3. In the referred

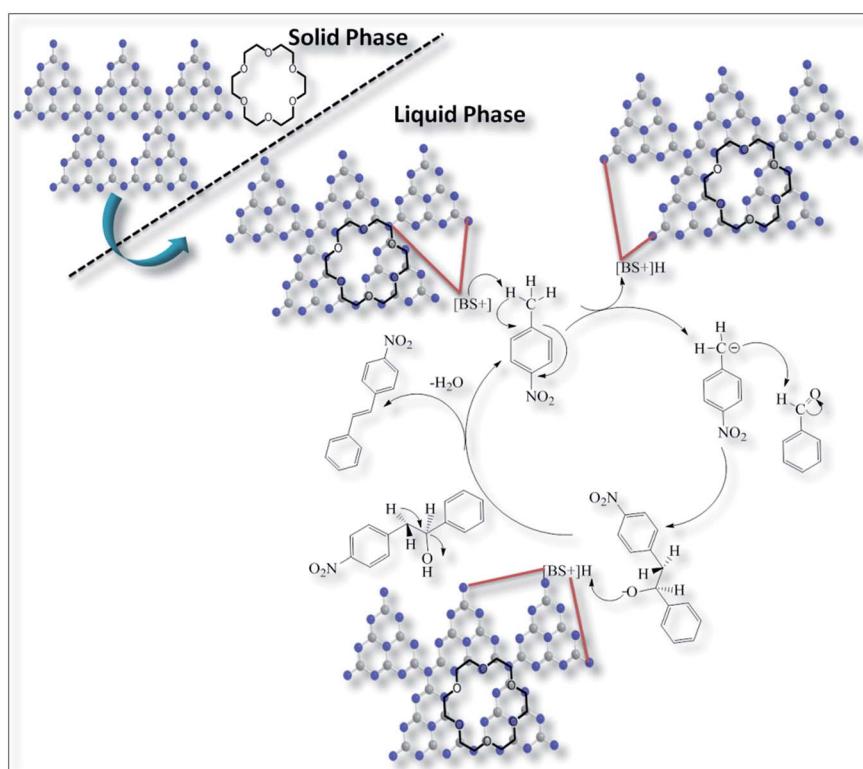


Knoevenagel condensation reaction under optimized conditions monosubstituted benzaldehyde reacted with 4-nitrotoluene, benzylcynide and 4-nitrobenzylcynide with 99% yield each respectively in a 30 min reaction time period (Table 3, entries 1, 2, 3). At the same time when disubstituted benzaldehyde reacts with monosubstituted another substrate *viz.*; benzylcynide the productivity of reaction is not affected and shows 85% of corresponding yield (Table 3, entry 5) of corresponding product (Table 3, entry 5, 6, 8). Since $-NO_2$ substituted electron rich substrates are considered to be strong candidate for enhancement of reaction progress (Table 3, entry 1-8). Further, disubstituted benzaldehyde reacted with disubstituted another substrate and shows excellent yield of (18Crown ether 6) exhibit excellent reactivity and not much affected by mono-substituted and disubstituted substrates (Table 3). It is clearly visualized from the Table 3 the synthesized $g\text{-}C_3N_4$ with phase transfer catalyst PTC (18Crown ether 6) efficiently affords moderate to excellent yields of the corresponding products for Knoevenagel condensation reaction.

After systematic protocol assigning for Knoevenagel condensation, we tried to explore a suitable mechanism involved in the system. According to the earlier reported mechanism, Knoevenagel condensation initiated with the deprotonation (either at higher temperature or with PTC) step from acidic site of substrate (*p*-nitro toluene) with the help of base.^{50,51,64} In the present study $g\text{-}C_3N_4$ catalyst with 18Crown ether 6 (PTC) is first time studied for the Knoevenagel condensation. The described reaction most probably might have followed the mechanism as shown in the Scheme 4.

However recently Junjie Guo *et al.* and co workers described the flexibility of graphene with 18Crown ether 6 and claims crown ethers (highly flexible, good binding affinity, and selective) embedded in graphene structure.⁶⁵ With the good agreement to the literature that graphene is analogous to $g\text{-}C_3N_4$ structure;⁶⁶⁻⁶⁹ therefore in the present study 18Crown ether 6 might have coordinated with $g\text{-}C_3N_4$ structure *via* owning rich flexibility and binding affinity for the easy availability of basic site (BS^+) in organic medium at room temperature. Further Lewis basic site of $g\text{-}C_3N_4$ deprotonate the acidic (H^+) from 4-nitrotoluene followed by attack of the carbanion on the electrophilic site of the benzaldehyde to yield the alcohol intermediate resulting subsequently to dehydration to form *E*-stilbene.

Nearly constant product yield was observed ($>84\%$) even after five recycling experiments, confirmed that the catalyst is stable and the basic nature of the synthesized $g\text{-}C_3N_4$ heterogeneous catalyst remains active (ESI: S10†) (Fig. 5). For further catalyst stability confirmation, FT-IR analyses of fresh $g\text{-}C_3N_4$ and spent $g\text{-}C_3N_4$ catalyst (five recycles) was carried out to probe the change of $g\text{-}C_3N_4$ at molecular level. The Fig. S8† shows the major peaks of $g\text{-}C_3N_4$ is well preserved even after the multiple reuses (1625, 1550, 1410 and 1250, 810, 3100 cm^{-1}). Further BET analysis result of spent $g\text{-}C_3N_4$ catalyst are as follows; BET surface area ($SBET$), total pore volume (V_p) and mean pore size (radius) $D_v(r)$ is, $23.22 \text{ m}^2 \text{ g}^{-1}$, $0.018 \text{ cm}^3 \text{ g}^{-1}$ 17.356 nm respectively. The observed increase in the surface area and pore size in spent catalyst, might be due to the transformation into monolithic sheets from bulk $g\text{-}C_3N_4$ *via* continues reuse (Fig. ESI 9†). Both the performed characterization suggesting



Scheme 4 Most probable scheme for Knoevenagel condensation by $g\text{-}C_3N_4$ by using PTC.



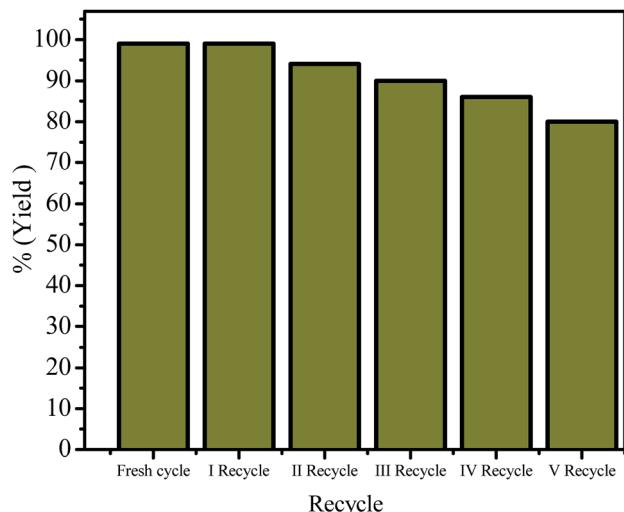


Fig. 5 Recycling study of heterogeneous catalyst $g\text{-C}_3\text{N}_4$ catalyst.

that the spent $g\text{-C}_3\text{N}_4$ catalyst remains unchanged at molecular level even after multiple reuses.

Conclusions

In a concluding remark, here we have demonstrated first time the use of $g\text{-C}_3\text{N}_4$ owning the basic and heterogeneous nature, with phase transfer catalyst for Knoevenagel condensation reaction. The catalytic performance is surprisingly enhanced due to use of phase transfer catalyst precisely 18Crown ether 6 (PTC) upto 99% yield within very short reaction time period (30 min) at room temperature with standard substrate. The newly established protocol for Knoevenagel condensation reaction is successfully screened with different substrate and demonstrated excellent product yield (>99%) at room temperature. The conducted experimental results demonstrate the basic nature of $g\text{-C}_3\text{N}_4$ efficiently activates the substrate at room temperature with PTC, which is responsible for the Knoevenagel condensation initiation. The exclusive salient feature of the successive protocol *via* $g\text{-C}_3\text{N}_4$ basic heterogeneous catalyst and phase transfer catalyst are; room temperature, short reaction time period (30 min), screening capability of various reactant, remains active under mild conditions and even after several reaction cycles.

Experimental

For graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) synthesis procedure sees ESI[†] for detail.

General procedure for the Knoevenagel condensation reaction

The reaction was carried out in a 25 mL oven dried, round bottom flask, with high magnetic stirring at ~800 rpm at room temperature. In a typical run, substrate 1 (4-nitrotoluene or similar kind) (1 mmol) and substrate 2 (benzaldehyde or similar kind) (1 mmol), at room temperature (25 °C) with PTC (0.1 mmol), solvent toluene (5 mL), $g\text{-C}_3\text{N}_4$ (30 mg) were allowed to stir. The reaction mixture samples were withdrawn periodically

at the measured time intervals and analyzed by gas chromatography. The samples were diluted and filtered with whatman paper before injecting into a gas chromatograph.

Acknowledgements

Author gratefully acknowledges Hani Gnayem & Ofer for their help to accomplish the present research work.

Notes and references

- 1 R. J. Davis, *J. Catal.*, 2003, **216**, 396–405.
- 2 M. J. Climent, A. Corma, R. Guil-Lopez, S. Iborra and J. Primo, *Catal. Lett.*, 1999, **59**, 33–38.
- 3 R. Radhakrishnan, D. M. Do, S. Jaenicke, Y. Sasson and G.-K. Chuah, *ACS Catal.*, 2011, **1**, 1631–1636.
- 4 R. A. Sheldon, *J. Mol. Catal. A: Chem.*, 1996, **107**, 75–83.
- 5 X. Liu, X. Piao, Y. Wang, S. Zhu and H. He, *Fuel*, 2008, **87**, 1076–1082.
- 6 H. Dabbagh and B. H. Davis, *J. Mol. Catal.*, 1988, **48**, 117–122.
- 7 H. Teterycz, R. Klimkiewicz and B. W. Licznerski, *Appl. Catal., A*, 2001, **214**, 243–249.
- 8 A. Corma and S. Iborra, in *Advances in Catalysis*, ed. C. G. Bruce and K. Helmut, Academic Press, 2006, vol. 49, pp. 239–302.
- 9 S. K. Kundu and A. Bhaumik, *RSC Adv.*, 2015, **5**, 32730–32739.
- 10 N. Linares, A. M. Silvestre-Albero, E. Serrano, J. Silvestre-Albero and J. Garcia-Martinez, *Chem. Soc. Rev.*, 2014, **43**, 7681–7717.
- 11 A. Corma, V. Fornés, R. M. Martín-Aranda, H. García and J. Primo, *Appl. Catal.*, 1990, **59**, 237–248.
- 12 V. Calvino-Casilda, R. M. Martín-Aranda, A. J. López-Peinado, I. Sobczak and M. Ziolek, *Catal. Today*, 2009, **142**, 278–282.
- 13 J. Roggenbuck and M. Tiemann, *J. Am. Chem. Soc.*, 2005, **127**, 1096–1097.
- 14 L.-B. Sun, X.-Q. Liu and H.-C. Zhou, *Chem. Soc. Rev.*, 2015, **44**, 5092–5147.
- 15 M.-A. Courtemanche, M.-A. Légaré, L. Maron and F.-G. Fontaine, *J. Am. Chem. Soc.*, 2013, **135**, 9326–9329.
- 16 V. B. Sapkal and B. M. Bhanage, *ChemSusChem*, 2016, **9**, 1980–1985.
- 17 B. List, *Chem. Rev.*, 2007, **107**, 5413–5415.
- 18 X. Chen, J. Zhang, X. Fu, M. Antonietti and X. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 11658–11659.
- 19 F. Su, S. C. Mathew, G. Lipner, X. Fu, M. Antonietti, S. Blechert and X. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 16299–16301.
- 20 S. Cao and J. Yu, *J. Phys. Chem. Lett.*, 2014, **5**, 2101–2107.
- 21 J. Wen, J. Xie, X. Chen and X. Li, *Appl. Surf. Sci.*, 2017, **391**, 72–123.
- 22 Y. Wang, X. Wang and M. Antonietti, *Angew. Chem., Int. Ed.*, 2012, **51**, 68–89.
- 23 S. Yin, J. Han, T. Zhou and R. Xu, *Catal. Sci. Technol.*, 2015, **5**, 5048–5061.





24 S. Patnaik, S. Martha, S. Acharya and K. M. Parida, *Inorg. Chem. Front.*, 2016, **3**, 336–347.

25 X. Jin, V. V. Balasubramanian, S. T. Selvan, D. P. Sawant, M. A. Chari, G. Q. Lu and A. Vinu, *Angew. Chem.*, 2009, **121**, 8024–8027.

26 X. Jin, V. V. Balasubramanian, S. T. Selvan, D. P. Sawant, M. A. Chari, G. Q. Lu and A. Vinu, *Angew. Chem., Int. Ed.*, 2009, **48**, 7884–7887.

27 S. van Dommele, K. P. de Jong and J. H. Bitter, *Top. Catal.*, 2009, **52**, 1575–1583.

28 M. B. Ansari, H. Jin, M. N. Parvin and S.-E. Park, *Catal. Today*, 2012, **185**, 211–216.

29 L. Zhang, H. Wang, W. Shen, Z. Qin, J. Wang and W. Fan, *Catal.*, 2016, **344**, 293–302.

30 Y. Wang, H. Li, J. Yao, X. Wang and M. Antonietti, *Chem. Sci.*, 2011, **2**, 446–450.

31 F. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. Wang and S. Blechert, *Angew. Chem., Int. Ed.*, 2011, **50**, 657–660.

32 X.-H. Li, J.-S. Chen, X. Wang, J. Sun and M. Antonietti, *J. Am. Chem. Soc.*, 2011, **133**, 8074–8077.

33 F. Su, M. Antonietti and X. Wang, *Catal. Sci. Technol.*, 2012, **2**, 1005–1009.

34 K. B. Becker, *Synthesis*, 1983, **1983**, 341–368.

35 T. P. Schultz, Q. Cheng, W. D. Boldin, T. F. Hubbard Jr, L. Jin, T. H. Fisher and D. D. Nicholas, *Phytochemistry*, 1991, **30**, 2939–2945.

36 T. P. Schultz, T. F. Hubbard Jr, L. Jin, T. H. Fisher and D. D. Nicholas, *Phytochemistry*, 1990, **29**, 1501–1507.

37 A. Roviello and A. Sirigu, *Makromol. Chem. Rapid Comm.*, 1982, **13**, 409–415.

38 E. C. Buruiana, T. Buruiana, G. Strat and M. Strat, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 1918–1928.

39 F. Silva, A. Figueiras, E. Gallardo, C. Nerín and F. C. Domingues, *Food Chem.*, 2014, **145**, 115–125.

40 C. J. Lion, C. S. Matthews, M. F. G. Stevens and A. D. Westwell, *J. Med. Chem.*, 2005, **48**, 1292–1295.

41 G. J. Soleas, E. P. Diamandis and D. M. Goldberg, *Clin. Biochem.*, 1997, **30**, 91–113.

42 T.-C. Hsieh and J. M. Wu, *BioFactors*, 2010, **36**, 360–369.

43 K. Ferré-Filmon, L. Delaude, A. Demonceau and A. F. Noels, *Coord. Chem. Rev.*, 2004, **248**, 2323–2336.

44 C. M. Kormos and N. E. Leadbeater, *J. Org. Chem.*, 2008, **73**, 3854–3858.

45 F. Alonso, P. Riente and M. Yus, *Eur. J. Inorg. Chem.*, 2009, **2009**, 6034–6042.

46 T. Banno, Y. Hayakawa and M. Umeno, *J. Organomet. Chem.*, 2002, **653**, 288–291.

47 S. Yousefi and A. R. Kiasat, *RSC Adv.*, 2015, **5**, 92387–92393.

48 N. Qafisheh, S. Mukhopadhyay and Y. Sasson, 2002.

49 S. Mukhopadhyay, G. Rothenberg, N. Qafisheh and Y. Sasson, *Tetrahedron Lett.*, 2001, **42**, 6117–6119.

50 M. Chidambaram, S. U. Sonavane, J. de la Zerda and Y. Sasson, *Tetrahedron*, 2007, **63**, 7696–7701.

51 Y. Sasson and G. Rothenberg, in *Handbook of Green Chemistry and Technology*, Blackwell Science Ltd, 2007, ch. 10, pp. 206–257, DOI: 10.1002/9780470988305.

52 G. Barak and Y. Sasson, *J. Org. Chem.*, 1989, **54**, 3484–3486.

53 J. Liu, T. Zhang, Z. Wang, G. Dawson and W. Chen, *J. Mater. Chem.*, 2011, **21**, 14398–14401.

54 F. Dong, L. Wu, Y. Sun, M. Fu, Z. Wu and S. C. Lee, *J. Mater. Chem.*, 2011, **21**, 15171–15174.

55 X. Chen, L. Zhang, B. Zhang, X. Guo and X. Mu, *Sci. Rep.*, 2016, **6**, 28558.

56 A. Kumar, P. Kumar, C. Joshi, S. Ponnada, A. K. Pathak, A. Ali, B. Sreedhar and S. L. Jain, *Green Chem.*, 2016, **18**, 2514–2521.

57 P. Sharma and Y. Sasson, *Green Chem.*, 2017, **19**, 844–852.

58 L. Song, S. Zhang, X. Wu, H. Tian and Q. Wei, *Ind. Eng. Chem. Res.*, 2012, **51**, 9510–9514.

59 S. Verma, R. B. Nasir Baig, M. N. Nadagouda and R. S. Varma, *ACS Sustainable Chem. Eng.*, 2016, **4**, 2333–2336.

60 F. Bigi, L. Chesini, R. Maggi and G. Sartori, *J. Org. Chem.*, 1999, **64**, 1033–1035.

61 L. F. Tietze, *Chem. Rev.*, 1996, **96**, 115–136.

62 J. C. Hogan and R. D. Gandour, *J. Am. Chem. Soc.*, 1980, **102**, 2865–2866.

63 J. C. Hogan and R. D. Gandour, *J. Org. Chem.*, 1992, **57**, 55–61.

64 N. Taha, Y. Sasson and M. Chidambaram, *Appl. Catal., A*, 2008, **350**, 217–224.

65 J. Guo, J. Lee, C. I. Contescu, N. C. Gallego, S. T. Pantelides, S. J. Pennycook, B. A. Moyer and M. F. Chisholm, *Nat. Commun.*, 2014, **5**, 5389.

66 Y. Zhang, Q. Pan, G. Chai, M. Liang, G. Dong, Q. Zhang and J. Qiu, *Sci. Rep.*, 2013, **3**, 1943.

67 G. Dong, Y. Zhang, Q. Pan and J. Qiu, *J. Photochem. Photobiol. C*, 2014, **20**, 33–50.

68 X. Dong and F. Cheng, *J. Mater. Chem. A*, 2015, **3**, 23642–23652.

69 V. N. Khabashesku, J. L. Margrave and J. L. Zimmerman, *Chem. Mater.*, 2002, **12**, 3264–3270.