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P_2O_5/SiO_2 as an efficient heterogeneous catalyst for the synthesis of heterocyclic alkene derivatives under thermal solvent-free conditions†

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A highly efficient methodology is developed for the synthesis of a series of heterocyclic alkene derivatives **3a–k** from 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde **1** and active methylene compounds **2a–k**, in the presence of P_2O_5/SiO_2, under thermal solvent-free conditions, in high yields, within a short reaction time. The catalyst is characterized for the first time by using X-ray diffraction (XRD), scanning electron microscopy–energy dispersive X-ray (SEM-EDX) and transmission electron microscopy (TEM). The stability of the catalyst is evaluated by thermogravimetric analysis/differential thermal analysis (TG/DTA) and differential scanning calorimetry (DSC) techniques. The molecular structure of alkene **3a** is confirmed by single crystal X-ray diffraction. The advantages of the present methodology are excellent yields of products, recyclability of the catalyst and an easy operational procedure.

1. Introduction

Heterogeneous catalysts have received considerable attention in organic synthesis because of environmental, economical, and industrial aspects. The use of solid heterogeneous catalysts for the development of clean processes is a theme of extreme importance in the chemical industry. These catalysts make the synthetic process economically viable as they can be easily recovered from the reaction mixture by simple filtration and can be reused several times to achieve very high turnover numbers compared to homogeneous catalysts.[1] Due to the highly corrosive, hazardous and polluting nature of liquid acids, the use of solid acid catalysts because of better regio- and stereoselectivity, low toxicity and high stability is gaining more importance in the chemical and refinery industries.[2] There are more than 100 industrial processes using over 103 solid acids as catalysts.[3]

As compared with their homogeneous analogues, immobilization of other catalytically active species on inorganic solid supports enables generation of recyclable catalysts which show higher catalytic activities, which may be due to the enhancement of substrate density around the active sites.[4] Because of the higher activity of the silica supported catalysts due to their larger surface area and better selectivity, they have become popular over the last two decades. In addition, silica supported reagents are promising for both academic and industrial applications due to their high mechanical and thermal stabilities, non-corrosivity and easy separation of the catalyst from the reaction mixture.[5,6]

Pyrazole derivatives are an attractive molecular scaffold for the search of new biologically active molecules. Studies reveal that incorporation of a pyrazole moiety into various heterocyclic ring systems gives worthwhile molecules from the biological point of view.[7–9] Several pharmaceutical drugs including celecoxib[10] and rimonabant[11] utilize the pyrazole as their core molecular entity.[12] Many pyrazole derivatives have a broad spectrum of biological activities, in particular, 5-chloropyrazole derivatives are reported to show potential antimicrobial,[13] analgesic and anti-inflammatory activity.[14] Moreover, 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde, which is used as starting material in the present study, possesses a halogen and aldehyde function in an ortho relationship and is a potential candidate for various organic transformations.[15,16]

A plethora of chemical methods have been reported for the formation of C═C bonds, which include Julia olefination,[17] Peterson olefination,[18] Ramberg–Backlund reaction,[19] Wittig reaction,[20] Wadsworth–Emmons reaction,[21] Wittig–Horner Reaction[22] and Knoevenagel condensation.[23] The Knoevenagel condensation is a facile and versatile method for the formation of carbon–carbon double bonds, with numerous applications in the synthesis of fine chemicals,[24] hetero-Diels–Alder reactions[25]

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and in the synthesis of carbocyclic as well as heterocyclic compounds of biological significance.[26] The reaction has been utilized in the preparation of coumarin derivatives,[27] cosmetics,[28] perfumes[29] and pharmaceutical chemicals.[30] The reaction is usually catalyzed by bases,[31] Lewis acids,[32] surfactants,[33] zeolites,[34] amine functionalized MCM-41,[35] amino functionalized mesoporous zirconia,[36] ionic liquids[37] *etc.* However, keeping in mind its own intrinsic worth, we decided to carry out further developments of this procedure in view of simplicity and environmentally benign and economic viability, as many of the reported methods suffer from drawbacks like complicated preparation of the catalyst, refluxing in hazardous organic solvents for prolonged time, use of expensive and toxic catalysts, high temperature and low product yields, harsh conditions with non-recyclable catalysts.

In continuation of our earlier studies on the development of new green protocols,[38,39] herein, we report for the first time a P_2O_5/SiO_2 catalyzed synthesis of heterocyclic alkene derivatives through Knoevenagel condensation under thermal solvent-free conditions (Scheme 2). In recent years, P_2O_5/SiO_2 has emerged as a promising heterogeneous solid acid catalyst in many organic transformations.[40–45] The advantages of using this catalyst are that it is inexpensive, easily preparable, stable, recyclable, and easily separable from the product.[46,47] The products are obtained in excellent yields within a short time period.

2. Experimental

2.1. Reagents

All starting materials of commercial grade were purchased from Sigma–Aldrich and used without further purification. P_2O_5 and SiO_2 were purchased from Merck. The purity of all compounds was checked by TLC on glass plates coated with silica gel (E-Merck G_{254}).

2.2. Apparatus and instruments

Melting points were determined on a Riechert Thermover instrument and are uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-300 and Bruker Avance 400 spectrometers. TMS was used as an internal standard and chemical shift values were in δ (ppm). The microanalytical data were collected on an Elementar vario EL III elemental analyzer. FT-IR spectra were obtained using a Perkin–Elmer spectrometer and done on KBr disc. The spectra were recorded in the 400–4000 cm^{-1} wave-number range. Mass spectra were obtained on a Jeol-SX-120 (FAB) and Micromass Quattro II (ESI). X-ray diffractograms (XRD) of the catalyst were recorded in the 2θ range of 10–70° (scan rate of 4° min^{-1}) on a Rigaku Miniflex X-ray diffractometer with Ni-filtered Cu Kα radiation at a wavelength of 1.54060 Å. The SEM-EDX analysis was obtained using a JEOL JSM-6510 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (acc. voltage: 20 kV) at different magnification and transmission and an electron microscope (TEM) using JEM-2100 F model (acc. voltage: 200 kV) with magnification up to 100 000×. Thermogravimetric/differential thermal analyses (TG/DTA) were obtained with a DTG-60H, with a heating rate of 25 °C min^{-1} from 100 to 1000 °C under N_2 atmosphere, and the differential scanning calorimetry (DSC) data obtained with a DSC-60 (Simultaneous DTA-TG Apparatus), Shimadzu (TGA) instrument with a heating rate of 20 °C min^{-1} from 0 to 500 °C under N_2 atmosphere. The X-ray single crystal diffraction of compound **3a** was performed on a BRUKER AXS SMART APEX diffractometer with a CCD area detector (MoKα = 0.71073 Å, monochromator: graphite).

2.3. Synthesis of the P_2O_5/SiO_2 catalyst

P_2O_5/SiO_2 was prepared by mixing P_2O_5 (1 mmol, 0.142 g) and 2 g of dried silica gel 60 (0.125–0.250 mm, previously heated at 120 °C for 24 h) in a mortar and grinding with a pestle to obtain a homogenous mixture as a white powder (2.142 g). This reagent is stable and can be kept at room temperature for months without loss of activity.[40]

2.4. General procedure for the Knoevenagel reaction

A mixture of 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde **1** (1.00 mmol), active methylene compounds **2a–k** (1.00 mmol) and **2l–n** (2.00 mmol), and 0.05g of P_2O_5/SiO_2 (7% *w*/*w*)[47] were mixed thoroughly using a mortar and pestle. The reaction mixture was then transferred to an open Pyrex 100 mL beaker and heated at 80 °C for the given time (Table 8). After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and ethyl acetate was added (5 mL). The reaction mixture was filtered to remove the catalyst and concentrated to furnish pure products **3a–n** (Scheme 2).

3. Results and discussions

3.1. Characterization of the P_2O_5/SiO_2 catalyst

The FT-IR spectrum of P_2O_5/SiO_2 (Fig. 1) showed the stretching band of SiO–H at 3299–3481 cm^{-1}, while the stretching and bending bands of P(O)OH appear at 2350, 1634 and 1068 cm^{-1}, respectively. The peak at 1230 cm^{-1} was assigned to the stretching of P=O and the peak at 1092 cm^{-1} attributed to Si–O–Si asymmetric band stretching vibrations. The low frequency modes at 794 cm^{-1} were due to the symmetric Si–O–Si stretching vibrations.[48] The adsorption peak at around 957 cm^{-1} showed the presence of a Si–O–P bond in the catalyst indicating the loading of P_2O_5 on the SiO_2 surface.

Formation of the catalytic system (P_2O_5/SiO_2) was identified by powder XRD (Fig. 2a). The XRD diffraction band at 2θ = 17°–28° was found to be broad indicating fine dispersion of P_2O_5 on the silica material and thus confirming the formation of amorphous P_2O_5–silica matrix.[49]

To study the surface morphology of the catalyst, SEM micrographs of the catalyst were employed. An examination of SEM images (Fig. 3) showed that P_2O_5 particles were of uneven shape and size, well distributed and no conglomeration of P_2O_5 particles was found on the surface of the silica gel. The increased reactivity of P_2O_5 supported on silica material

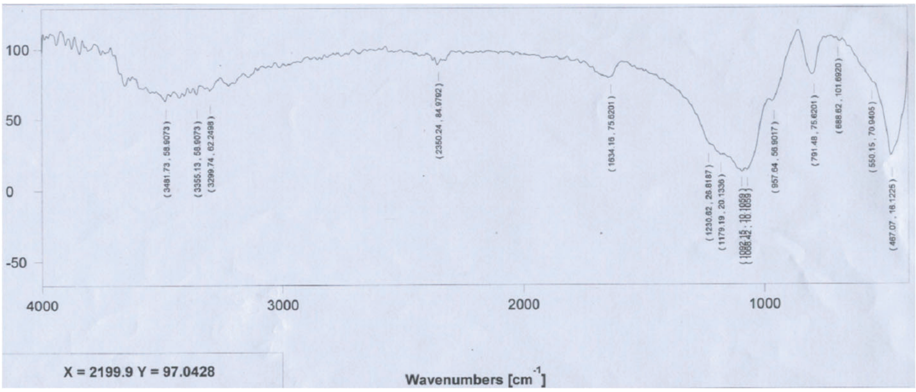


Fig. 1 FT-IR spectra of P_2O_5/SiO_2 catalyst.

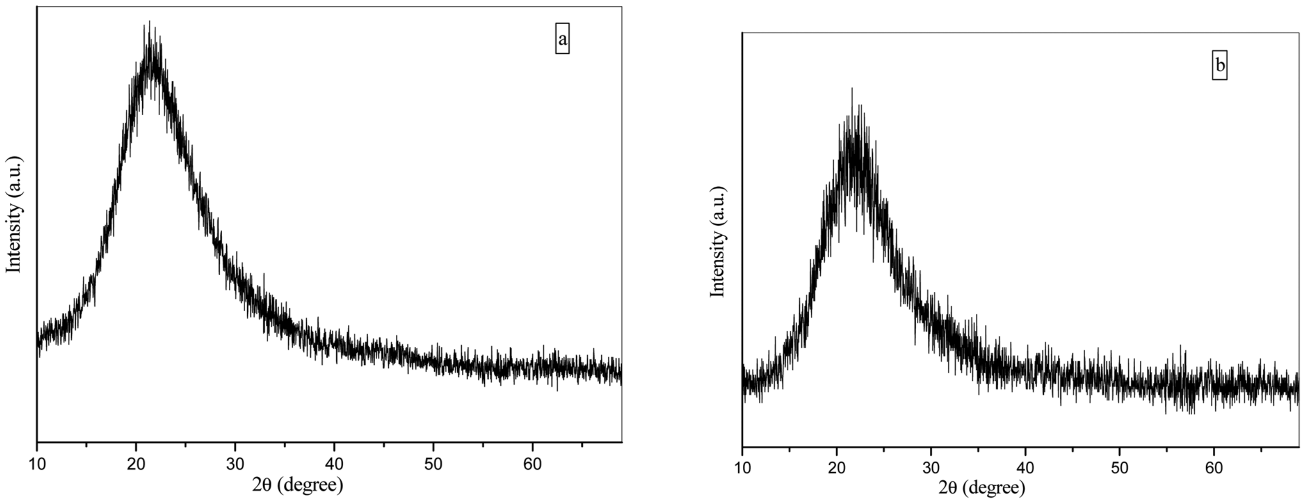


Fig. 2 (a) Powder XRD of fresh P_2O_5/SiO_2. (b) Powder XRD of P_2O_5/SiO_2 after five runs.

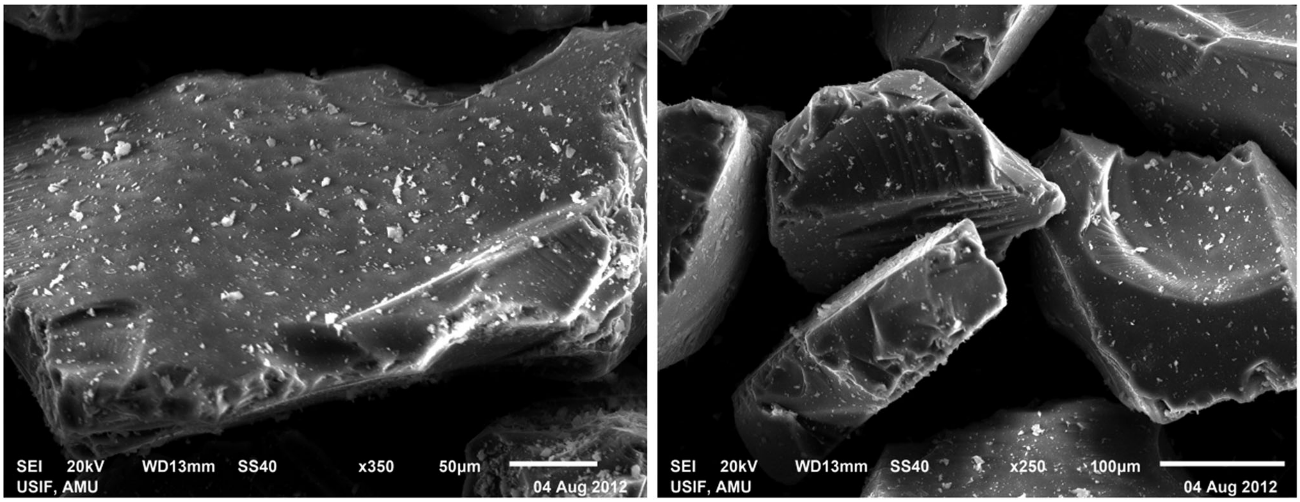


Fig. 3 SEM images of P_2O_5/SiO_2 catalyst at different magnifications.

could be possibly due to the catalyst–support interactions, and the resultant changes in the surface properties of the reactive sites.

TEM image (Fig. 4) further showed uniform distribution of P_2O_5 particles as black dots on the surface of silica, confirming the formation of the expected catalyst.

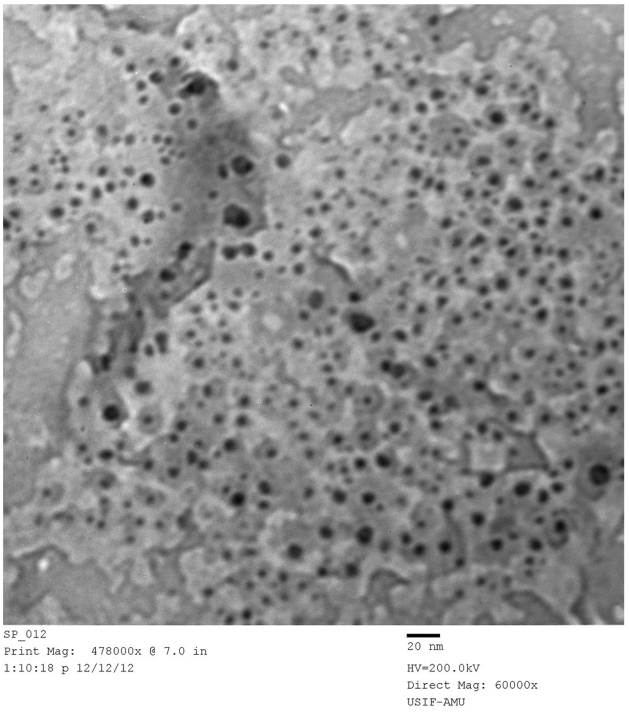
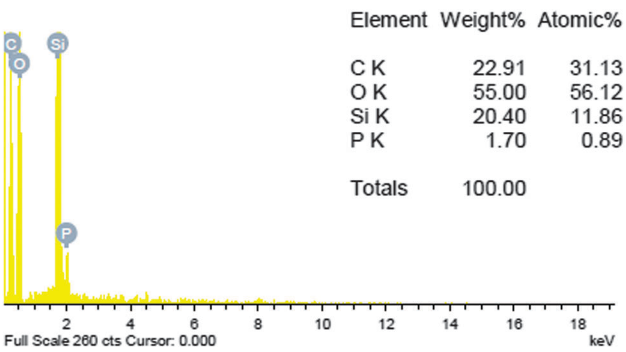


Fig. 4 TEM image of P_2O_5/SiO_2 catalyst.

Further confirmation for the formation of the expected catalytic system was done by EDX analysis (Fig. 5) which showed the presence of Si, O and P elements.

To estimate the thermal stability of P_2O_5/SiO_2, TG/DTA and DSC experiments were carried out. A weight loss (about 14%) was observed in the DTA curve (Fig 6a) between 42 °C and 133 °C with an endothermic peak at around 85.55 °C which can be attributed to the evaporation of residual water molecules. In the TGA graph (Fig 6a) no apparent weight loss after weight loss of 14% was observed indicating the stability of the catalyst. The DSC curve (Fig 6b) showed an irreversible endothermic transition at 113 °C, which may be due to the loss of adhered water molecules trapped in silica gel framework.

To the best of our knowledge, there is no report on the characterization of the catalyst (P_2O_5/SiO_2) using XRD, SEM-EDX and TEM studies and the stability of the catalyst using TG/DTA and DSC analysis.



Element	Weight%	Atomic%
C K	22.91	31.13
O K	55.00	56.12
Si K	20.40	11.86
P K	1.70	0.89
Totals	100.00	

Fig. 5 EDX analysis of the fresh catalyst (P_2O_5/SiO_2).

3.2. Evaluation of catalytic activity of P_2O_5/SiO_2 for the synthesis of heterocyclic alkene derivatives

In order to optimize the reaction conditions, including temperature, solvents, catalysts, loading of catalyst, and supports in terms of yield and time, the reaction of 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde **1** with 1, 3-dimethyl barbituric acid **2a** was selected as a model reaction.

First the reaction was carried out under grinding at room temperature without any catalyst. The reaction took longer time for completion (6 h) with trace amounts of the product being generated. Then the reactions were conducted at 25, 50, 80 and 100 °C in the presence of P_2O_5/SiO_2 as catalyst (Table 1). The yield of the product increased from 43% to 99% as the temperature was raised from 25 to 80 °C. A further increase in the temperature up to 100 °C did not show any effect. Therefore, 80 °C was chosen as the optimal temperature for all further reactions.

To evaluate the efficiency as well as capacity of the solvent-free conditions in comparison with solvent conditions, the model reaction was examined in the presence of P_2O_5/SiO_2 in different solvents such as CH_3CN, CH_2Cl_2, $CHCl_3$, THF, MeOH, EtOH, H_2O and dioxane. When the reaction was performed in EtOH and MeOH, a moderate yield of the product (**3a**) was obtained after a longer time period (Table 2, entry 2, 3) whereas in the presence of CH_3CN, CH_2Cl_2, $CHCl_3$, H_2O, THF and dioxane, only trace amounts of the product were obtained (Table 2, entry 4–9). The same reaction was then carried out using P_2O_5/SiO_2 in solvent-free conditions at room temperature. The reaction was completed within 1 h, but the yield of the product was not satisfactory (43%). When the reaction was performed in solvent-free conditions at 80 °C in the presence of P_2O_5/SiO_2, it was completed within 2 min with a considerable increase in the yield of the product (99%) (Table 2). In a comparative study using other green solvents, the model reaction was also performed in PEG-400 and glycerol and it was observed that the reaction was completed in relatively shorter times but with mixture of products (entry 10, 11). Thus, our study revealed that solvent-free conditions are best for the P_2O_5/SiO_2 catalyzed synthesis of heterocyclic alkene derivatives in terms of reduced reaction times and excellent yields of the products.

To establish the superiority of P_2O_5/SiO_2 over other heterogeneous catalysts, the model reaction was carried out in the presence of different catalysts. Our investigation revealed that the catalytic activity of various acidic/basic catalysts in solvent-free conditions was in the order P_2O_5/SiO_2 > $NaHSO_4$–SiO_2 > Chitosan > NH_4OAc–SiO_2 > $NaHSO_4$–alumina (acidic) > $NaHSO_4$–alumina (basic) > $NaHSO_4$–alumina (neutral) in terms of time and yield. (Table 3). It is thus clear that P_2O_5/SiO_2 (7% *w*/*w*) exhibited the highest catalytic activity with regard to the transformation of heteroaldehyde **1** and active methylene **2a–k** into substituted electrophilic alkenes **(3a–k).**

In order to prove the efficiency of P_2O_5/SiO_2 for the Knoevenagel condensation, a comparison with other reported catalysts was also made (Table 4). In the presence of P_2O_5/SiO_2 the product

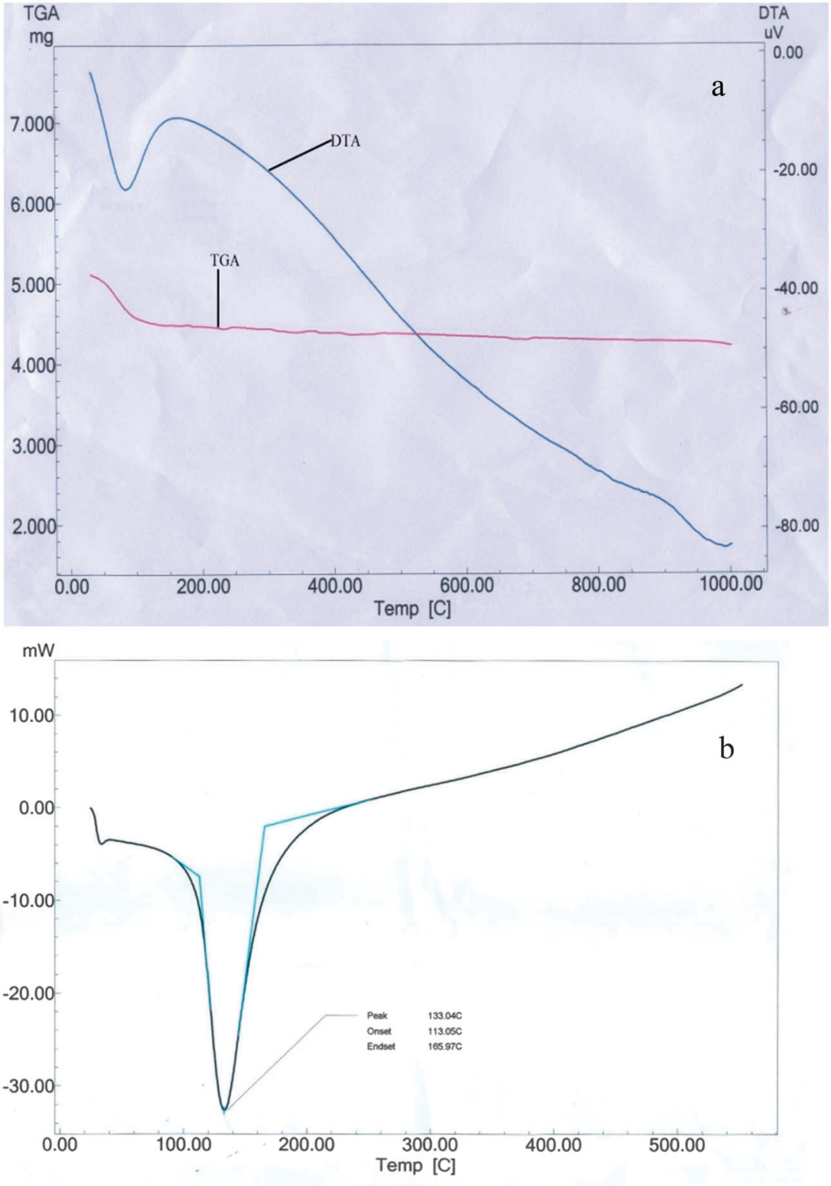


Fig. 6 (a) TG/DTA graph of P_2O_5/SiO_2. (b) DSC of P_2O_5/SiO_2.

Table 1 Effect of temperature on the synthesis of **3a** in thermal solvent-free conditions[a]

Entry	Temperature (°C)	Time[b] (min)	Yield[c] (%)
1	25	60	43
2	50	15	78
3	80	2	99
4	100	2	99

[a] *Reaction conditions*: 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde (1.0 mmol), 1,3-dimethyl barbituric acid (1.0 mmol), catalyst 0.05 g, T = 80 °C. The reaction work-up was carried out as detailed under Section 2. [b] Reaction progress monitored by TLC. [c] All yields refer to isolated yield.

(**3a**) was obtained in excellent yield (99%) within short times (2 min) whereas with other reported catalysts Knoevenagel condensation products were obtained in varying yields (88–98.2%) and times (5 min–10 h). It is thus clear from the table that P_2O_5/SiO_2 is superior to other catalysts in terms of time, yield and reaction conditions. The work-up procedure is very simple and no further purification is required for obtaining the pure products. The higher activity of P_2O_5/SiO_2 as compared to other reported catalysts may be due to the heterogeneous nature of the catalyst and the thermal solvent-free conditions. A plausible mechanism for the Knoevenagel condensation is depicted in Scheme 1.

The activity of different loadings of P_2O_5 on silica support was also investigated for the synthesis of **3a** by using 3.5, 7 and 10.5% *w*/*w* of P_2O_5 supported on SiO_2 (Table 5). With 3.5% *w*/*w* P_2O_5/SiO_2 lower yields of the product were obtained in longer times (Table 5, entry 1) whereas with 10.5% *w*/*w* P_2O_5/SiO_2

Table 2 Effect of various solvents *versus* solvent-free on the synthesis of **3a** in the presence of P_2O_5/SiO_2[a]

Entry	Solvent	Time[b]	Yield[c] (%)
1[d]	Solvent-free	2 min	99
2	EtOH	1.30 h	60
3	MeOH	1.45 h	57
4	CH_3CN	2 h	Trace
5	CH_2Cl_2	2.15 h	Trace
6	CH_3Cl	4 h	Trace
7	H_2O	5.10 h	Trace
8	THF	5.18 h	Trace
9	Dioxane	5.25 h	Trace
10	PEG-400	4.16 h	49 (mixture)
11	Glycerol	3.44 h	52 (mixture)

[a] *Reaction conditions*: 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde (1.0 mmol), 1,3-dimethyl barbituric acid (1.0 mmol), catalyst 0.05 g, T = 80 °C. The reaction work-up was carried out as detailed under Section 2. [b] Reaction progress monitored by TLC. [c] All yields refer to isolated yield. [d] Thermal solvent-free conditions.

Table 3 Effect of various heterogeneous catalysts on the synthesis of **3a** in thermal solvent-free conditions[a]

Entry	Catalyst	Time[b] (min)	Yield[c] (%)
1	P_2O_5/SiO_2	2	99
2	$NaHSO_4$–SiO_2	25	80
3	Chitosan	33	71
4	NH_4OAc–SiO_2	40	65
5	$NaHSO_4$–alumina (acidic)	49	54
6	$NaHSO_4$–alumina (basic)	65	38
7	$NaHSO_4$–alumina (neutral)	78	32

[a] *Reaction conditions*: 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde (1.0 mmol), 1,3-dimethyl barbituric acid (1.0 mmol), catalyst 0.05 g, T = 80 °C. The reaction work-up was carried out as detailed under Section 2. [b] Reaction progress monitored by TLC. [c] All yields refer to isolated yield.

again the yield was not satisfactory (Table 5, entry 3). An excellent yield of the product was obtained with 7% *w*/*w* P_2O_5/SiO_2 (Table 5, entry 2). The lower activity of 3.5% *w*/*w* P_2O_5 loaded silica is possibly attributable to the lower ratio of P_2O_5 to silica whereas the lower activity of 10.5% *w*/*w* P_2O_5 loaded silica could be due to multi layer P_2O_5 on the support.

In evaluating the effect of catalyst concentration, the best yield was obtained in the presence of 0.05 g P_2O_5/SiO_2. No significant improvement in the yield was observed on increasing the loading to 0.075 and 0.1 g, whereas, decreasing the amount of catalyst to 0.025 g resulted in a lowering of the yield (Table 6).

To establish the use of silica as the best support for P_2O_5, other supports were also investigated (Table 7). To evaluate the role of SiO_2, the model reaction was carried out in solvent-free conditions at 80 °C in the presence of P_2O_5 alone. We found that the yield using P_2O_5/SiO_2 was greater (average, 30%) than for P_2O_5 alone under the same conditions whereas with acidic, basic and neutral alumina under similar reaction conditions

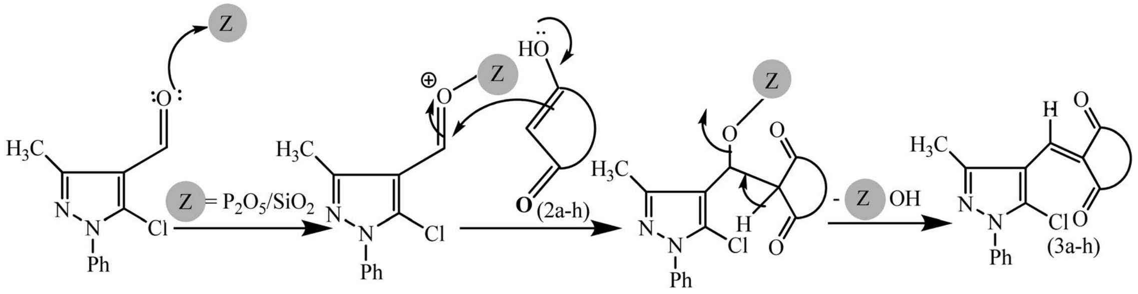
Table 5 Effect of P_2O_5 loading on the support for the synthesis of **3a** in thermal solvent-free conditions[a]

Entry	P_2O_5/SiO_2 (% *w*/*w*)	Time[b] (min)	Yield[c] (%)
1	3.5	7	78
2	7	2	99
3	10.5	2	82

[a] *Reaction conditions*: 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde (1.0 mmol), 1,3-dimethyl barbituric acid (1.0 mmol), catalyst 0.05 g, T = 80 °C. The reaction work-up was carried out as detailed under Section 2. [b] Reaction progress monitored by TLC. [c] All yields refer to isolated yield.

Table 4 Comparison of the results obtained with other reported catalysts for the Knoevenagel condensation products

Entry	Catalyst	Conditions	Time	Yield (%)	Ref.
1	P_2O_5/SiO_2	Solvent-free/80 °C	2 min	99	Present work
2	NH_4OAc–SiO_2	Dichloromethane	6 h	90	50
3	Sulfuric acid–SiO_2	RT	6 h	88	51
4	Guanidine	Dichloromethane	10 h	97.3	52
5	L-Proline	Ethanol	40 min	98	53
6	$HClO_4$–SiO_2	Water	30 min	91	54
7	Potassium sorbate	US	8 min	98.2	55
8	Amino functionalized mesoporous silica	Ethanol	5 h	95	56
9	HAP-γ-Fe_2O_3[Bmim]OH	Water	1 h	98	57
10	In/AlMCM-41	Ethanol	25 min	95	58
11	NH_4OAc	MW	5 min	94	59
12	Zn[(L-proline)2]	MW	6 min	95	60



Scheme 1 Plausible mechanism for the Knoevenagel condensation.

Table 6 Effect of catalyst loading on the synthesis of **3a** in thermal solvent-free conditions[a]

Entry	P_2O_5/SiO_2 (g)	Time[b] (min)	Yield[c] (%)
1	0.025	8	76
2	0.05	2	99
3	0.075	2	99
4	0.1	2	99

[a] *Reaction conditions*: 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde (1.0 mmol), 1,3-dimethyl barbituric acid (1.0 mmol), catalyst 0.05 g, T = 80 °C. The reaction work-up was carried out as detailed under Section 2. [b] Reaction progress monitored by TLC. [c] All yields refer to isolated yield.

Table 7 Effect of different supports on the synthesis of **3a** in thermal solvent-free conditions[a]

Entry	Support	Time[b] (min)	Yield[c] (%)
1	—	17.5	67
2	Silica gel	2	99
3	Acidic Alumina	4	79
4	Basic Alumina	4.5	65
5	Neutral Alumina	5.5	53

[a] *Reaction conditions*: 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde (1.0 mmol), 1,3-dimethyl barbituric acid (1.0 mmol), catalyst 0.05 g, T = 80 °C. The reaction work-up was carried out as detailed under Section 2. [b] Reaction progress monitored by TLC. [c] All yields refer to isolated yield.

the yield was moderate to good (Table 7, entry 3–5). It is thus clear from the table that SiO_2 as a support is superior to other supports in terms of time and yield. The effect of SiO_2 may be due to good dispersion of P_2O_5 on the surface of silica gel leading to significant improvements in its reactivity.

The scope and generality of this environmentally benign method was further demonstrated by the reaction of heterocyclic aldehyde **1** with different active methylene compounds **2a–k** under solvent-free condition. All the reactions proceeded smoothly and were completed within 2–9 min to afford the products **3a–k** in excellent yields (95–99%) (Table 8). However, the reaction of heteroaldehyde **1** with triacetic acid lactone **2l**, 6,7-dimethyl-4-hydroxycoumarin **2m** and 4-hydroxycoumarin **2n** did not give the expected Knoevenagel condensation products; instead, it afforded pyrazolo pyrones **3l**, **3m** and **3n** in a very short time (Table 8). The structure of newly synthesised compound **3m** was confirmed on the basis of spectral analysis (FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectra). The IR spectrum of **3m** showed sharp and strong absorption bands at 1726 cm^{-1} and 3377 cm^{-1} for the carbonyl and hydroxyl groups of the coumarin moiety, respectively. Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) exhibited sharp singlets at δ 2.34, δ 2.39 and δ 2.43 for the methyl groups of the pyrazole and coumarin moiety, respectively. Another singlet integrating for one proton at δ 7.07 was assigned to the methine proton.

Table 8 P_2O_5/SiO_2 catalyzed Knoevenagel condensation under thermal solvent-free conditions[a]

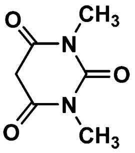
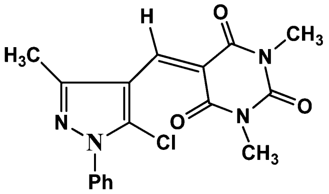
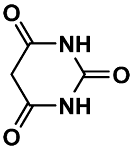
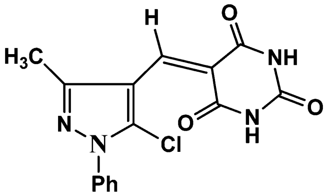
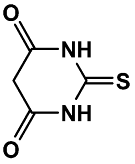
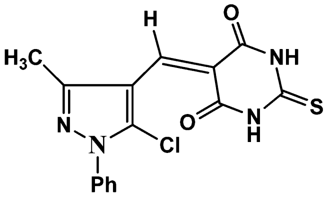
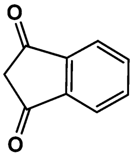
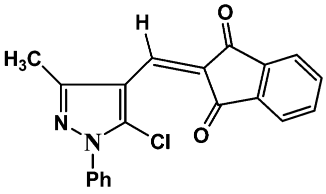
Entry	2a–n	Product	Time (min)	Yield[d] (%)
3a[b]			2	99
3b[b]			3	98
3c[b]			6	97
3d[b]			4	97

Table 8 (*continued*)

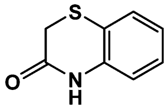
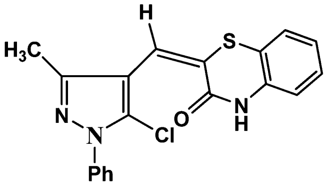
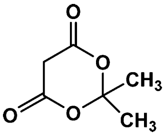
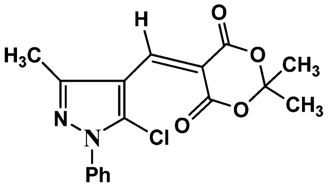
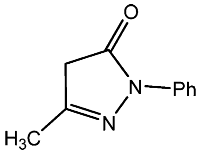
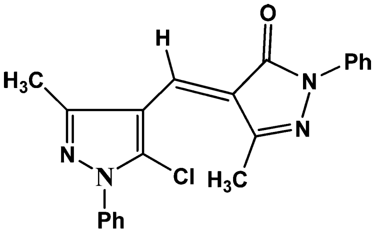
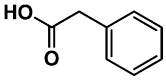
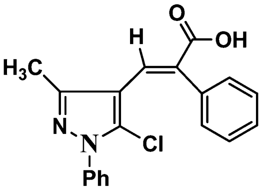
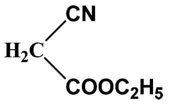
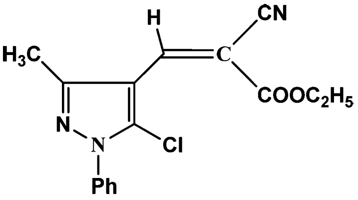
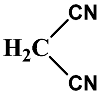
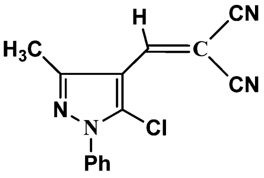
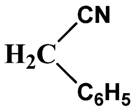
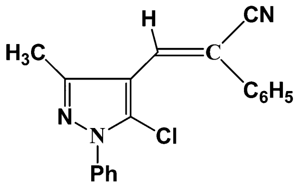
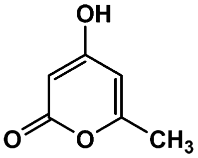
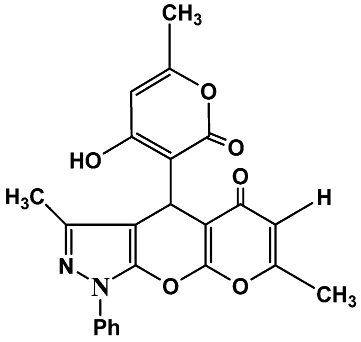
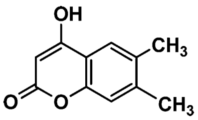
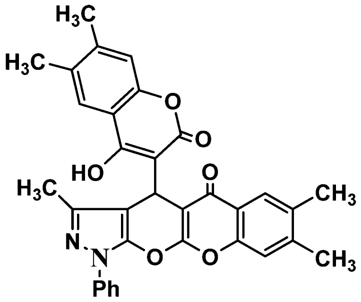
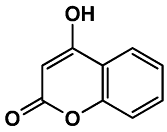
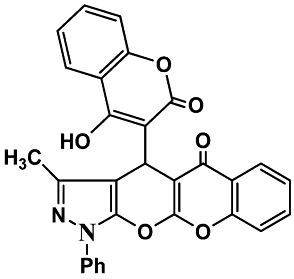
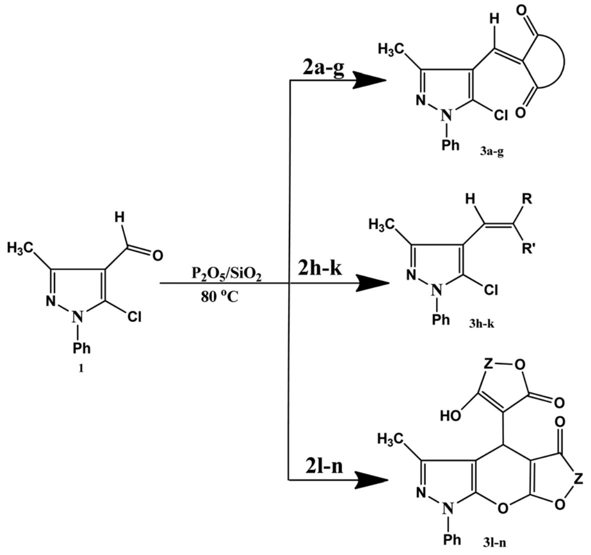
Entry	2a–n	Product	Time (min)	Yield[d] (%)
3e[b]			9	95
3f[b]			8	96
3g[b]			5	98
3h[c]			3	98
3i[b]			5	96
3j[b]			3	98
3k[b]			2	98

Table 8 (*continued*)

Entry	2a–n	Product	Time (min)	Yield[d] (%)
3l[b]			4	95
3m[c]			3	96
3n[b]			4	95

[a] *Reaction conditions*: 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde (1.0 mmol), different active methylene compounds **2a–k** (1.0 mmol) and **2l–n** (2.00 mmol), catalyst 0.05 g, $T = 80$ °C. The reaction work-up was carried out as detailed under Section 2. [b] The products were confirmed by melting points and compared with reported literature.[60,61] [c] New compounds. [d] All yields refer to isolated yield.

Nine aromatic protons appeared as a multiplet in the region δ 7.34–8.35. The ^{13}C NMR spectrum showed signals at δ 183.17 and δ 166.52 for the hydroxyl and carbonyl carbons of the coumarin moiety, respectively, and other carbon signals appeared at their appropriate positions. Further confirmation of the structure was provided by mass spectrometry which showed $M^+ + 1$ at m/z 547.



Scheme 2 Synthesis of **3(a–n)** under thermal solvent-free conditions.

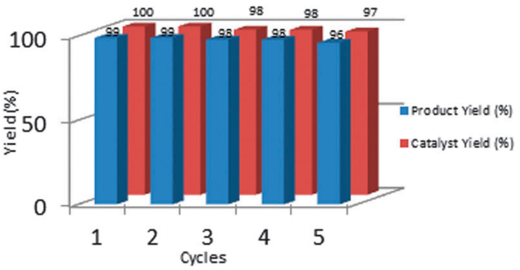


Fig. 7 Recyclability of the catalyst for the model reaction.

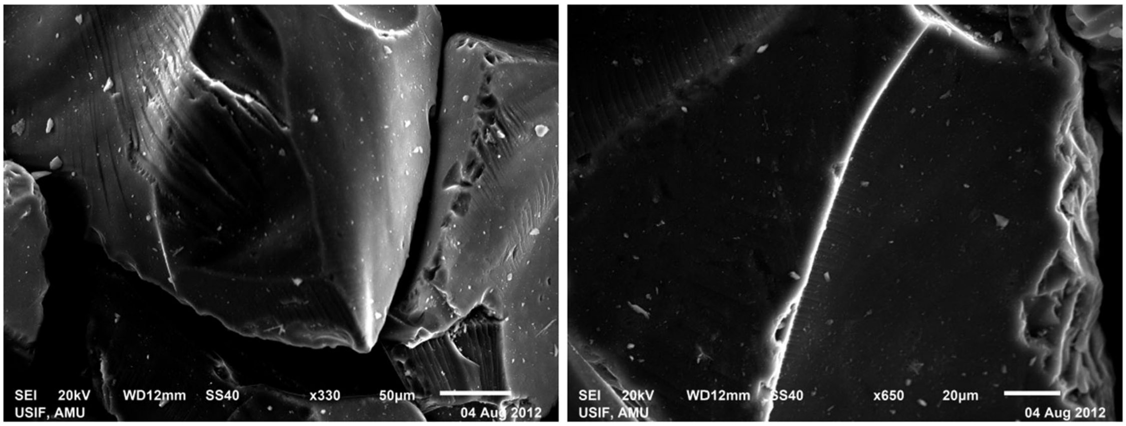
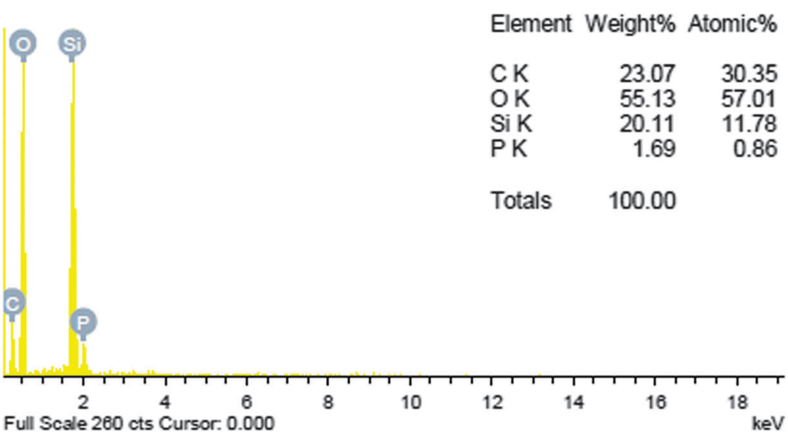


Fig. 8 The SEM image of recovered catalyst after five runs at different magnifications.



Element	Weight%	Atomic%
C K	23.07	30.35
O K	55.13	57.01
Si K	20.11	11.78
P K	1.69	0.86
Totals	100.00	

Fig. 9 EDX analysis of the recovered catalyst after five runs (P_2O_5/SiO_2).

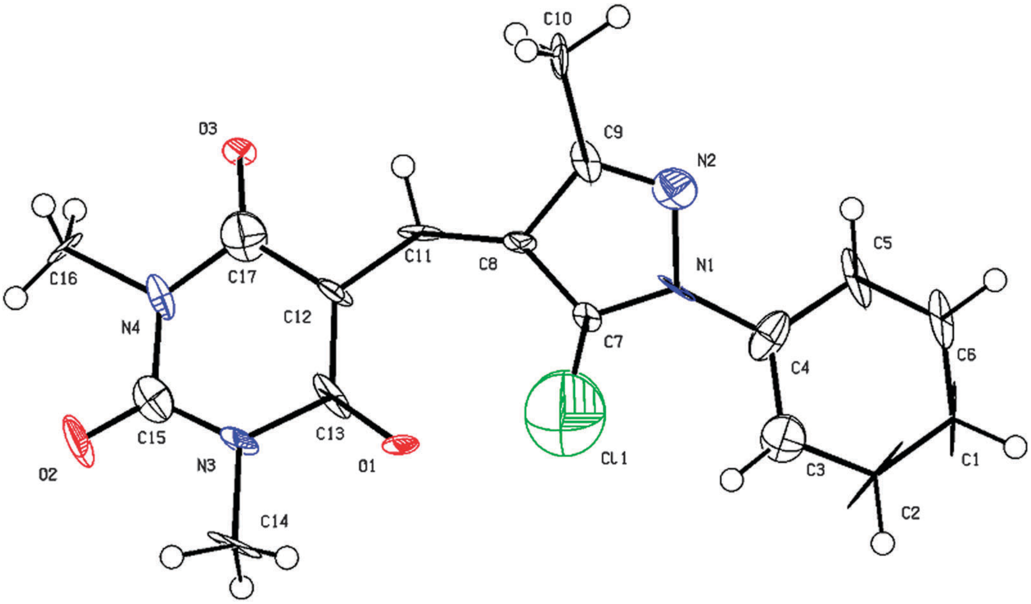


Fig. 10 ORTEP structure of the Knoevenagel condensation product (**3a**), with 30% probability of thermal ellipsoids.

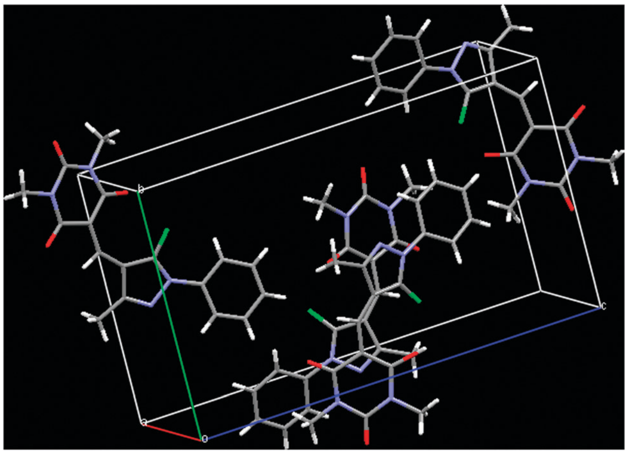


Fig. 11 Packing diagram of the product **3a**.

A recyclability test of the catalyst was performed in order to satisfy the green chemistry criteria. The solid catalyst recovered after the reaction by filtration was washed twice with ethyl acetate (5 mL × 2), and activated at 100 °C under static conditions for 2 h. Fresh quantities of **1** and **2a** were used and the obtained catalyst was reused in the next reaction cycle. The catalyst was successfully reused five times under similar reaction conditions giving high conversions in the range 96–99%, without any significant change in the catalytic activity and morphology of the catalyst even after five reaction cycles (Fig. 7). The recycling result suggests heterogeneity of the catalyst. It is worth mentioning here that for every cycle the catalyst was tested for the reaction at microscale.

The identity of the recovered catalyst was checked by powder XRD and SEM-EDX analysis. It was assessed that the peaks remained the same (Fig. 2b), and also there was no change in the morphology of the catalyst (Fig. 8 and 9) as compared to the fresh catalyst.

The structure of compound **3a** was confirmed by single crystal X-ray data. The molecular structure is shown in Fig. 10. The structure consists of a discrete monomeric unit. It is clear from the crystal structure of the compound that a Knoevenagel reaction has taken place and the desired heterocyclic alkene derivative between 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde and 1,3-dimethyl barbituric acid has been formed. The atoms are not all in a single plane as seen from Fig. 10. The bond length of *d* C11–C12 = 1.419 Å (which is near the length of a C=C bond) in the final product confirms the existence of a double bond. No hydrogen bonding or π–π interactions are observed between the neighbouring units of the present molecule in order to form a supramolecular framework (Fig. 11) (CCDC deposit No. 846722).

4. Conclusions

In summary, this paper describes a convenient and highly efficient process for the synthesis of heterocyclic alkene derivatives under thermal solvent-free conditions using P_2O_5/SiO_2 as an efficient catalyst. The present protocol offers attractive features such as excellent yields of the products in short times, simple work-up procedure, environmentally benign and economic viability and reusability of the catalyst. We believe that this method provides a better scope for the synthesis of heterocyclic alkene derivatives through Knoevenagel condensation and will be a more practical alternative to the other existing methods.

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