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$BiCl_3$-modified perlite as an effective catalyst for selective organic transformations: a green protocol

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Abstract

A new perlite supported Bismuth Chloride ($BiCl_3$) was used as an efficient heterogeneous catalyst for the synthesis of heterocyclic compounds viz., quinoxalines and dihydropyrimidinones. Fourier-transform infrared spectroscopy (FT–IR), scanning electron microscopy, energy dispersive spectra, X-ray diffractometry, thermogravimetric analysis and Brunauer–Emmett–Teller surface area analytical techniques were employed to characterize the prepared catalyst. Initially, the catalytic activity of the prepared $BiCl_3$-Perlite was tested towards synthesis of simple quinoxaline derivatives at room temperature. The effect of solvent in the preparation of quinoxaline was also examined. The formed products were confirmed by their physical (melting point) and spectral data (FT–IR, ^1H and ^{13}C-NMR). In order to implement the activity of the $BiCl_3$-Perlite catalyst, a multicomponent reaction was adopted for synthesis of dihydropyrimidinones under solvent free conditions in a micro oven. The use of recyclable heterogeneous solid acid catalyst makes the reaction simple with minimum chemical waste, shorter reaction time, easy workup and products in good yield.

Keywords $BiCl_3$-Perlite · Heterogeneous catalyst · Solvent free · Quinoxalines · Dihydropyrimidinones

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Introduction

Catalyst plays a major role in green chemistry by receiving considerable importance in minimizing pollution towards growing environmental concerns. Owing to the essentials of green technology, extensive significance is given to solid acid catalyst as an alternative for homogeneous catalyst. Even though homogeneous catalyst viz., $ZnCl_2$ [1], Phosphoric acid [2], $AlCl_3$ [3], $[Al(H_2O)_6](BF_4)_3$ [4], $CuCl_2{\cdot}2H_2O$ [5], trifluoroacetic acid [6], Baker's yeast [7], phosphate ester [8], molecular iodine [9] etc., have been used in versatile organic reactions, they suffer from flaws like prolonged reaction time, generation of acidic waste, expensive catalyst and non-recoverable. To overcome these difficulties, heterogeneous solid acid catalysts [10–15] have been advanced in modern days that are known to be economical, non-corrosive and of easy regeneration.

In addition, multicomponent reactions provides alternate routes to existing methodology, in which at least three starting materials are involved in a single step leading to a product with high atom economy. And so, the significance of MCR reactions is evident from its prevalent application in various reactions [16–25] including synthesis of imidazoles [26, 27], oxadiazoles [28–30], chromenes [31, 32], quinoxalines [33], thiazolidinones [34], quinolones [35], pyridines [36] and pyrroles [37].

Perlite is a naturally occurring mineral oxide with 70–75% of SiO_2, 12–18% of Al_2O_3, 3–4% of Na_2O, 3–5% of K_2O, 0.5–2% of Fe_2O_3, 0.2–0.7% of MgO, and 0.5–1.5% of CaO [38]. It is an environmentally benign mineral oxide known for high porosity and adsorbability, good chemical and thermal resistance, less toxicity, low cost, light weight, ease of handling [39–42] and, furthermore, it finds a noteworthy role as catalyst in several reactions [43, 44]. $BiCl_3$ has been used as a Lewis acid catalyst in different kinds of organic reactions such as the hetero Diels–Alder reaction [45], β-amino carbonyl compounds [46], reductive amination [47], allylation of carbonyl compounds [48] and ring opening of epoxides with aromatic amines [49]. However, $BiCl_3$ is hard to deal with because of its hygroscopic nature, and it also causes severe respiratory and gastrointestinal track burns. To succeed in handling $BiCl_3$ and considering the significance of perlite, an attempt has been made to synthesize $BiCl_3$-Perlite as a novel heterogeneous solid acid catalyst in multicomponent reactions.

An article, montmorillonite K10 clay supported $BiCl_3$, as an effective solid acid catalyst for the preparation of bis(indolyl)methanes and azines [50, 51] marked that the acidity of $BiCl_3$–MK10 was approximately 18 times larger than simple MK10. Consequently, inclusion of $BiCl_3$ to the clay material will enhance the acidity of the clay and facilitates the acid catalyzed reaction. The present study involves the preparation and characterization of $BiCl_3$-Perlite acid catalyst and validating the effectiveness of the catalyst towards the preparation of pharmacologically active heterocycles. Quinoxalines are acknowledged for its extensive pharmacological activities as anti-tubercular [52], antibacterial [53], anticancer [54], anti-inflammatory [55] and antimalarial [56]. Dihydropyrimidinones (DHPMs) are recognized for their antitumeral [57], anti-inflammatory [58],

antiviral [59], calcium channel inhibitors [60] and antioxidant [61] activities. The aforesaid properties of these heterocycles provoked us to an emphasis on synthesis of quinoxalines and dihydropyrimidinones.

Experimental

General

All the chemicals used were procured from Merck and used as received. The synthesized catalyst was characterized by Scanning Electron Microscopy (SEM) using a JEOL 6390 equipped with an Energy Dispersive X-ray spectrometer (EDX), X-ray Diffraction patterns were acquired utilizing a SCHIMADZU XRD-6000 Japan diffractometer with Cu Kα irradiation (λ = 1.5416 Å) operating at 20kv, thermal stability of $BiCl_3$-perlite catalyst was resolved by Differential Scanning Calorimetry-Thermo Gravimetric Analysis (DSC-TGA) from 50 to 800 °C by heating rate of 10 °C/min under nitrogen purge using a SDTQ 600 V20.9 Build 20 instrument, surface area was verified using the Brunauer–Emmett–Teller (BET) method. The structure of the as-prepared compounds were characterized by an infrared spectrum recorded in aSCHIMADZU FT–IR spectrometer, ^{1}H and ^{13}C NMR spectra were obtained from a BRUCKER 400 MHz spectrometer using $CDCl_3$/DMSO as solvent containing 0.1 TMS.

Preparation of perlite powder

In order to eliminate organic impurities, about 10 g of perlite powder was suspended in 200 mL of ethanol by vigorous stirring for 10 h. The obtained residue was filtered and washed with ethanol and heated in aqueous solution of 5 N NaOH for 30 min. The resulting bare perlite was then filtered and rinsed with excess water to remove NaOH and allowed to dry at 120 °C for 48 h.

Preparation of $BiCl_3$-Perlite

A new catalyst ($BiCl_3$-Perlite) was prepared by a simple dispersion method. About 2.7 g of perlite is suspended in 50 mL of 2-propanol, 0.135 g of $BiCl_3$ was dispersed in 10 ml of 2-propanol and added dropwise into the suspension of perlite-2-propanol under vigorous stirring. Stirring was continued for a further 4 h at room temperature to obtain the $BiCl_3$-Perlite composite. Then a fine powder of $BiCl_3$-perlite was obtained after drying at 110 °C for 3 h. This catalyst contained 5 wt% $BiCl_3$. Similarly catalysts with 1, 2, 3, 4 & 6 wt% were prepared by adapting the same procedure with different concentrations of $BiCl_3$.

General procedure for synthesis of quinoxalines

The mixture of various diamines (0.001 mol) and benzil (0.001 mol) in ethanol (3–5 mL) with 0.1 g of catalyst was stirred at room temperature for about 5 to 50 min. The reaction progress was examined using thin layer chromatography (TLC) with hexane as solvent. At the point of completion, the insoluble catalyst was filtered, and the product was separated by adding ethyl acetate. The crude product obtained by evaporating the solvent was purified by recrystallization using ethanol as solvent. The structure of the compounds was confirmed by FT–IR, ^{1}H NMR & ^{13}C NMR spectral analysis.

General procedure for synthesis of dihydropyrimidinones

Aldehyde (0.001 mol), urea (0.0015 mol), ethylaceto acetate (0.001 mol) and 0.0125 g of $BiCl_3$-Perlite were taken in dry media and irradiated under a microwave oven at 400 W for 5–20 min. Completion of the reaction was affirmed by TLC using hexane and ethyl acetate as eluting mixture. Then ethyl acetate was added to the reaction mixture, then the catalyst was filtered and washed with solvent for further use. The crude product obtained by evaporating the solvent was purified by recrystallization using ethanol as solvent. Structure of the synthesized compounds was confirmed by IR and NMR spectral techniques.

Results and discussion

Catalyst characterization

The synthesized solid acid catalyst was characterized by FT–IR, SEM, EDS, XRD, DSC-TGA and BET surface area measurements.

To assess the successful immobilization of bismuth chloride on perlite FT–IR spectra of pure perlite and $BiCl_3$-Perlite (5 wt%) were recorded. IR spectrum of perlite Fig. S1 (see Supplementary material), shows five significant absorption bands. The indicative bands corresponding to stretching and bending modes of OH groups on the perlite surface (mainly Si–OH groups) and adsorbed water molecules were depicted at 3572 cm^{-1} and 1635 cm^{-1}, respectively. The peaks observed at 1056 cm^{-1} and 786 cm^{-1} were assigned to Si–O stretching vibrations of O–Si–O and Si–O–Al, respectively. Moreover, O–Si–O bending vibrations were evident at about 457 cm^{-1}. The additional peak at 1484 cm^{-1} in the IR spectrum of $BiCl_3$-perlite (Fig. S2) was attributed to stretching vibration of $BiCl_3$.

The surface morphology of pure perlite and modified perlite was studied by SEM technique.

Figure 1 represents the selected SEM images of pure perlite (a) and $BiCl_3$-Perlite (b). The successful functionalization of $BiCl_3$ over perlite was indicated by surface roughness in comparison with pure perlite which exhibited

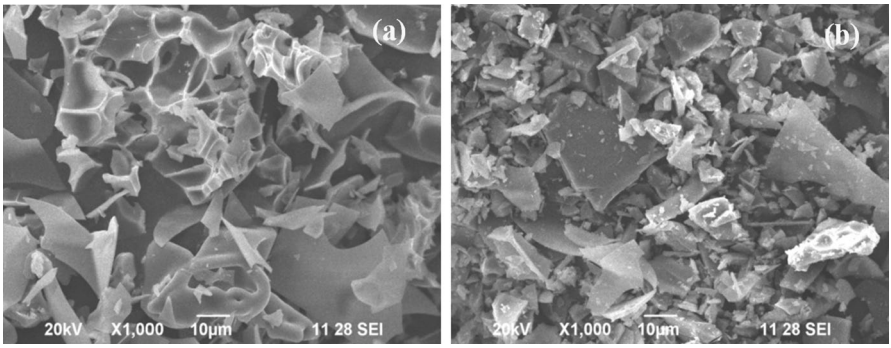


Fig. 1 SEM images of **a** Pure Perlite and **b** $BiCl_3$-Perlite

a smooth layer-like structure. Figure 2 depicts the energy dispersive spectra of pure Perlite (Fig. 2a) and $BiCl_3$-Perlite (Fig. 2b). The presence of elements Si, Al, K, Na, Ca, Fe, O was evident in the EDS analysis for both pure perlite and $BiCl_3$-Perlite. The existence of additional peaks at 2, 2.5 and 3.5 confirmed the effective immobilization of $BiCl_3$ on pure perlite. The percentage composition of elements was given in Table 1 for both perlite and $BiCl_3$-Perlite. About 4.6% of bismuth in $BiCl_3$-Perlite confirmed that $BiCl_3$—perlite was formed with good elemental composition.

The X-ray diffraction patterns were measured to investigate the crystalline nature of pure perlite and $BiCl_3$-Perlite catalysts which were furnished in Fig. 3. The broad peak at 2θ value of 26º indicated the amorphous nature of perlite (Fig. 3a). The XRD pattern of $BiCl_3$-Perlite (Fig. 3b) was unique in relation to that of pure Perlite, the additional peaks at 2θ values of 25.9°, 32.5°, 33.4°, 46.6°, 58.6° [62] were attributed to Bi which confirmed effective loading of $BiCl_3$.

Thermogravimetric analysis of $BiCl_3$-Perlite was recorded to explore the thermal stability of the synthesized solid acid catalyst. DSC-TGA curves of $BiCl_3$-Perlite are represented in Fig. 4. The results demonstrated an initial mass loss of 3.75% at 120 °C which was corresponding to the removal of adsorbed water molecules. A second gradual mass loss of 5% from 130 to 500 °C indicates a slow mass loss of the $BiCl_3$ group. The third mass loss of 3.12% from 500 to 550 °C was attributed to sudden mass loss of $BiCl_3$. Further mass loss at higher temperature might be expected to cause dehydroxylation of Perlite. Whereas, TGA of pure Perlite reported in the literature [63] showed a mass loss below 120 °C due to loss of water molecules and a steady weight loss was observed up to 600 °C, attributed to gradual dehydroxylation of Perlite.

Surface area measurement, exposed that the surface area, pore volume and pore diameter of $BiCl_3$-Perlite is larger than that of pure Perlite (Table 2). The average surface area, pore volume and pore diameter are about 2.2862 m^2/g, 4.247×10^{-3} cm^3/g and 6.9893 nm for modified perlite and 1.7014 m^2/g, 2.240×10^{-3} cm^3/g and 2.2774 nm for pure perlite, respectively.

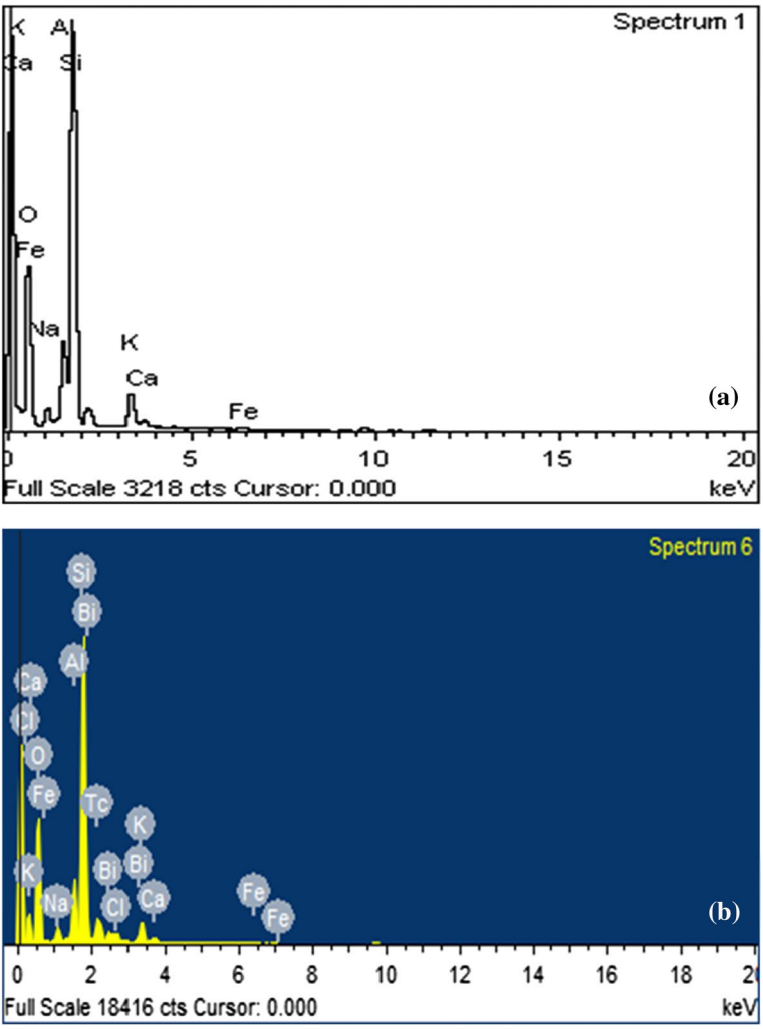


Fig. 2 EDS of **a** Pure Perlite and **b** $BiCl_3$-Perlite

Table 1 Percentage of elements present in Perlite and $BiCl_3$-Perlite

Samples	Si	Al	K	Na	Fe	Ca	Bi
Perlite	71.20	11.05	4.33	3.09	1.04	0.82	–
$BiCl_3$-Perlite	71.05	11.03	4.28	3.10	1.01	0.79	4.63

Optimization of $BiCl_3$ on Perlite for synthesis of quinoxaline derivatives

To find out the optimum concentration of $BiCl_3$ on Perlite, the condensation of 1,2-phenylene diamine and benzil was carried out at room temperature with bare

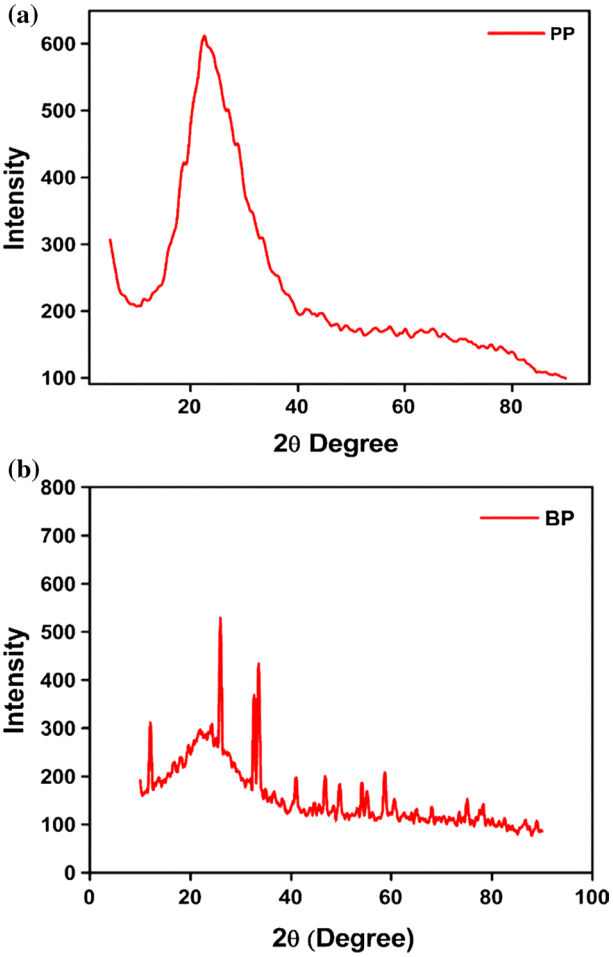


Fig. 3 XRD patterns of **a** Pure Perlite and **b** $BiCl_3$-Perlite

perlite and $BiCl_3$-perlite with different concentrations of $BiCl_3$ in ethanol medium (Scheme 1). Percentage yield of quinoxaline with different catalysts was given in Table 3. The yield of quinoxaline with bare perlite is observed to be 80.5%. 5 wt% of $BiCl_3$-Perlite gave 98.2% yield which is to be most efficient. When $BiCl_3$ concentration increased to more than 5 wt%, the yield decreased. Hence, 5 wt% $BiCl_3$ was fixed as the optimum level. Conversely, this reaction gave no trace of product when performed without catalyst in ethanol. In order to find the effect of solvent, the reaction between 1,2-diphenylenediamine and benzil was carried out in different solvents viz., ethanol, acetonitrile and water under the same reaction conditions (Table 4). The reaction was completed in 5 min with 98.2% and 95.3% yield in solvents ethanol and acetonitrile, respectively. It was identified that the same reaction in water required a longer time to give 85% yield of product in Table 4. Owing to

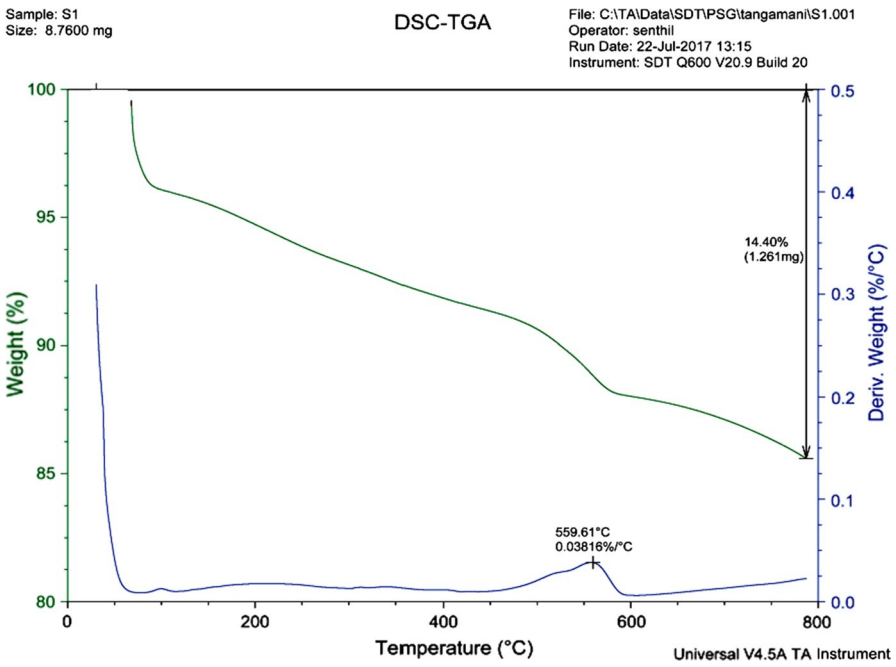
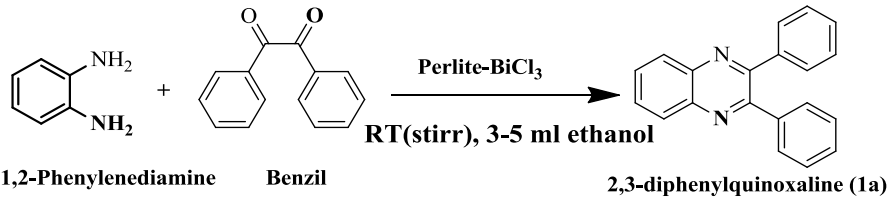


Fig. 4 DSC-TGA of $BiCl_3$-Perlite

Table 2 Pore parameters of Perlite and $BiCl_3$-Perlite

Samples	BET surface area (m^2/g)	Pore volume (cm^{-3}/g)	Pore diameter (nm)
Pure-Perlite	1.7014	2.24×10^{-3}	2.277
$BiCl_3$-perlite	2.2862	4.247×10^{-3}	6.9893



Scheme 1 Condensation reaction of 1,2-phenylenediamine and benzil

maximum yield of product in minimum time, ethanol was selected as a suitable solvent for other reactions.

The effect of catalyst amount on synthesis of quinoxaline was studied by changing the catalyst amount from 0.05 to 0.2 g (Fig. 5). Owing to increase in number of particles of catalyst the yield of quinoxaline increases from 94.0 to 98.2%, when

Table 3 Optimization of $BiCl_3$ on Perlite for the synthesis of 2,3-diphenylquinoxaline in ethanol medium

Entry	Catalysts	[a]Yield (%)
1	Bare Perlite	80.5
2	1 wt% $BiCl_3$-Perlite	92.3
3	2 wt% $BiCl_3$-Perlite	95.5
4	3 wt% $BiCl_3$-Perlite	96.9
5	4 wt% $BiCl_3$-Perlite	97.3
6	5 wt% $BiCl_3$-Perlite	98.2
7	6 wt% $BiCl_3$-Perlite	96.3

[a]Isolated yield

Table 4 Solvent effect on the synthesis of 2,3-diphenylquinoxaline with 5 wt% $BiCl_3$-Perlite at room temperature

Entry	Solvent	Time(min)	[a]Yield (%)
1	C_2H_5OH	5	98.2
2	CH_3CN	5	95.3
3	H_2O	20	85

[a]Isolated yield

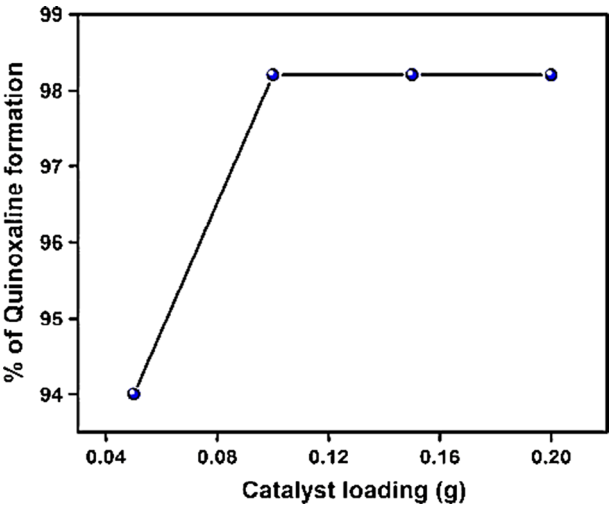
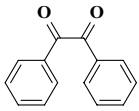
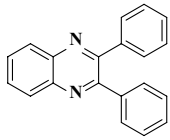
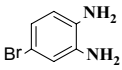
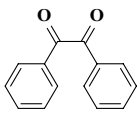
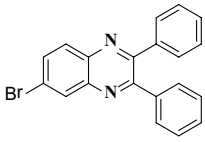
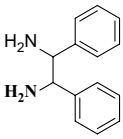
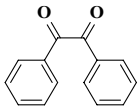
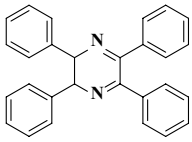
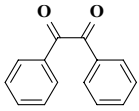
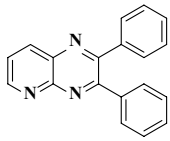
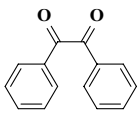
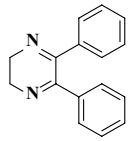


Fig. 5 Effect of catalyst loading for quinoxaline synthesis

the catalyst amount was varied from 0.05 to 0.1 g. There was no significant change in conversion that occurred when the catalyst amount was increased beyond 0.1 g. Thus, the optimum catalyst loading was observed to be 0.1 g for the synthesis of quinoxalines. Motivated by significant results obtained in the above reactions, this protocol was extended to synthesis of various quinoxalines from different 1,2-diamines, and the results obtained are summarized in Table 5. *o*-phenylenediamine with

Table 5 Quinoxaline derivatives from different 1,2-diamines and benzil with 5 wt% $BiCl_3$-Perlite catalyst under room temperature in ethanol

Entry	1,2-Diamine	1,2-Diketone	Product	Time (min)	[a]Yield (%)
1a				5	98.2
1b				20	97.6
1c				45	80.4
1d				50	83.7
1e				50	87.3

[a]Isolated yield

electron withdrawing group gave slightly lower yield of products with longer reaction time in comparison with simple *o*-phenelenediamine (Table 5, entry 1b). Reaction with other diamines (Table 5, entries 1c and 1d) and aliphatic diamine (Table 5, entry 1e) also produced product in reasonable yields. Structure of the products was determined by spectral data (Figs. S3–S17, see Supplementary material). Correspondingly, reactions with substituted 1,2-phenylenediamines and with other diamines progressed neatly at room temperature in an ethanol medium and no objectionable side products were formed. As reported earlier this condensation reaction followed the same mechanism for acid catalyzed condensation reactions [64, 65].

The catalyst reusability in ethanol was inspected for the reaction of *o*-phenylenediamine with benzil. At the point of completion, product was recovered by adding

Table 6 Reusability of $BiCl_3$-Perlite in the synthesis of 2,3-diphenylquinoxaline

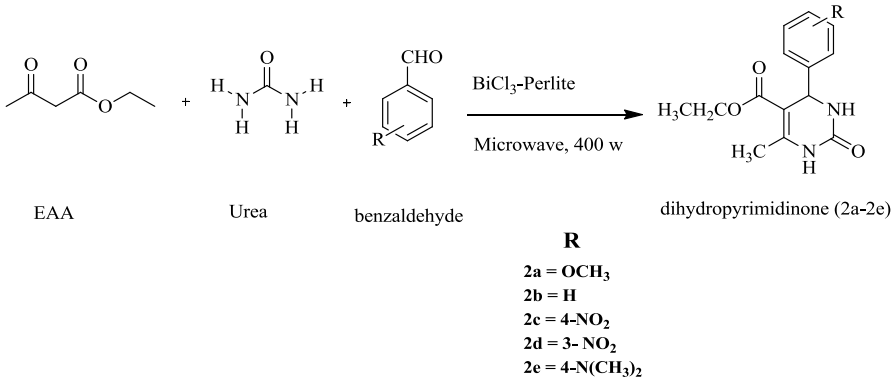
Run	1	2	3	4	5
[a]Yield (%)	98.0	97.0	96.0	94.0	94.0

[a]Isolated yield

Table 7 Catalytic performance of reported catalyst with the present work

Entry	Catalyst	Condition	Time (min)	Yield	References
1	Fe_3O_4@SiO_2–imid–PMA	Stirring (rt)	5–45	77–97	[42]
2	polymer supported sulphanilic acid	Stirring (rt)	40–52	80–88	[43]
3	sulfated polyborate	Stirring (100 °C)	5–10	96–99	[44]
4	$SbCl_3/SiO_2$	Stirring (rt)	5–45	70–98	[45]
5	ZrO_2/Ga_2O_3/MCM-41	Stirring (rt)	120	83–97	[46]
6	[TMPSA]. H_2SO_4	Stirring (rt)	15–30	70–92	[47]
7	$BiCl_3$-Perlite/solvent Free	Stirring (rt)	5–50	80–98	Present work

rt room temperature



Scheme 2 Condensation reaction of EAA, Urea and aldehyde

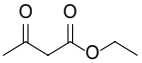
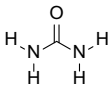
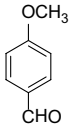
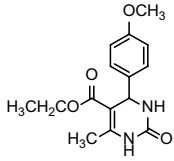
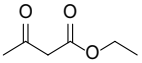
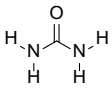
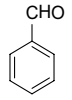
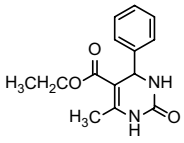
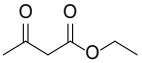
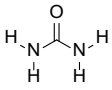
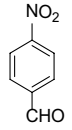
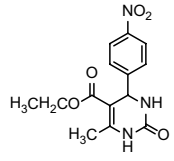
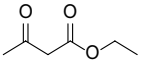
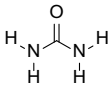
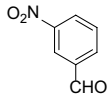
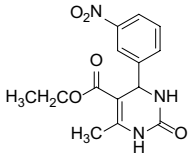
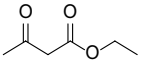
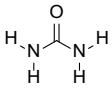
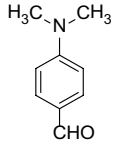
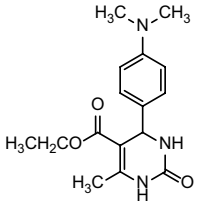
ethyl acetate. Then the catalyst was filtered, dried and reused. The regenerated catalyst could be reused five times lacking no significant loss in its catalytic activity (Table 6).

The effectiveness of $BiCl_3$-perlie was explored by comparing with reported catalyst (Table 7). The results revealed that the suggested catalyst was reliably notable concerning other catalysts reported in literature.

Solvent free synthesis of dihydropyrimidinones and optimization process

Synthesis of DHPMs was performed by the reaction of aldehyde (0.001 mol), urea (0.0015 mol) & EAA (0.001 mol) with a catalytic amount of 5 wt% $BiCl_3$-Perlite as solid acid catalyst (Scheme 2) under microwave irradiation for about 8–20 min,

Table 8 Percentage formation of DHPMs derivatives from EAA, Urea and different aldehydes using 5 wt% $BiCl_3$-Perlite under microwave irradiation

Entry	EAA	Urea	Aldehyde	Structure	Time (min)	[a]Yield (%)
2a					10	95
2b					20	89
2c					20	94
2d					8	95
2e					15	92

[a]Isolated yield

and gave 89–95% of yield (Table 8). However, no reaction was observed when it was irradiated without catalyst for 10 min, and further increase of irradiation time resulted in charring. Similarly, condensation was also carried out under the same conditions with bare perlite and the product yield was only 65% at 10 min.

The influence of catalyst loading on formation of DHPMs was studied by varying the catalyst amount from 0.075 to 0.2 g (Fig. S18). When the catalyst amount was increased from 0.075 to 0.125 g, the yield of the product was increased from 86 to 95%. Above 0.125 g, no significant change in the yield of product was noticed. Thus

Table 9 Catalytic performance of reported catalyst with the present work

Entry	Catalyst	Condition	Time (min)	Yield	References
1	Si-MCM-41-$FeCl_3$/Solvent Free	MW (700 W)	3–5	70–98	[48]
2	ZrO_2-pillared clay/Solvent Free	MW (630 W)	5–7	85–97	[49]
3	$FeCl_3$/nanopore silica/Solvent Free	MW (400 W)	12–15	36–73	[50]
4	$H_3PMo_{12}O_{40}$)/Solvent Free	MW (900 W)	5–13	76–95	[51]
5	SBA-15/SF	100° C	20–75	65–94	[52]
6	$SnCl_2$/nano SiO_2	Reflux	38–48	68–97	[53]
7	$BiCl_3$-Perlite/solvent Free	MW (400 W)	8–20	89–95	Present work

the optimum catalyst loading was found to be 0.125 g. Similar reaction was investigated with different substituted aldehydes to identify the versatility of the proposed protocol and the % yields are summarized in Table 8. For many substituents the product obtained was more than 90%. We found that electron releasing and electron withdrawing groups almost proceeded with similar yield. FT–IR, ^{1}H NMR and ^{13}C NMR studies were performed to confirm the structure of the synthesized compounds (Figs. S19–S33, see Supplementary material).

The reusability was examined to study the practical application of this catalyst. Completion of the reaction was tested by TLC, ethyl acetate was added to the reaction medium, and then catalyst was separated by filtration, dried and reused for further reactions. The separated catalyst was reused four times with no considerable change in yield. The catalyst was observed to be effective after each reaction, which indicated that the $BiCl_3$ was stable and reusable (Table S1). The outcome of the catalyst was compared with literature references (Table 9). These results evidently proved that $BiCl_3$—perlite catalyst is strongly equal or much more effective for the Biginelli reaction.

Conclusion

In summary, we successfully introduced $BiCl_3$-Perlite as a novel, simple and eco-friendly heterogeneous solid acid catalyst for the synthesis of quinoxalines and dihydropyrimidinones.

A new clay-based solid acid catalyst, $BiCl_3$-Perlite, was prepared by simple solid dispersion method, and it was characterized by FT–IR, SEM, EDS, XRD, TGA and BET surface area measurements. XRD and EDS confirm the $BiCl_3$ loading on Perlite. The optimum catalyst loading was identified as 0.1 g and 0.125 g for quinoxalines and dihydropyrimidinones, respectively. Utilization of this $BiCl_3$-Perlite catalyst offers many benefits such as good to excellent activity for the condensation reaction at room temperature. Another attractive feature was that the catalyst can be separated from the reaction medium easily and can be reused several times without losing its significant catalytic activity.

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