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Nanocrystalline 5 % Fe/ZnO as an efficient catalyst for quinoxaline synthesis

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Abstract Various 2-aryl quanoxalines were synthesized with good yields from *o*-phenylene diamines and phenacyl bromides in one pot using novel nanocrystalline 5 % Fe/ZnO catalyst, at room temperature. The salient feature of this method includes mild reaction conditions, short reaction time, good yield, high purity of product, and recyclable catalyst without noticeable decrease in catalytic activity, which can be used for large-scale synthesis. The synthesized 5 % Fe/ZnO nanoparticles were characterized by using XRD, SEM, and TEM techniques.

Keywords 5 % Fe/ZnO · *o*-Phenylene diamines · Phenacyl bromides · Quinoxaline · Room temperature · Recyclable catalyst

Introduction

Quinoxaline nucleus is an important pharmacophore in modern drug design and discovery [1]. The substituted quinoxaline derivatives have been reported in a wide range of applications in diverse therapeutic areas, including anti-inflammatory, antiviral, antibacterial, antiprotozol, anticancer, antidepressant, antiHIV, and antitumor [2–4]. Quinoxaline moieties are present in the various antibiotics such as echinomycin, levomycin, and antinoleutin, which are known to inhibit the growth of Gram-positive bacteria and are active against various transplantable tumors [5]. Quinoxalines are also used for technology up-gradation and also serve as useful rigid subunits in macrocyclic receptors in molecular recognition [6–9]. The widespread applications of quinoxaline containing structure have prompted studies on their synthesis.

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Numerous methods are available for the synthesis of quinoxaline and DHP's (dihydropyrazines) involving condensation of 1,2-diamines with 1,2 dicarbonyl compound, aryl ketones using $ZrOCl_2$, $NbCl_4$, and HDNIB in PEG [10–12], bi-catalyzed oxidative coupling of epoxides with 1,2-diamines [13], heteroannulation of nitroketene N, S-aryliminoacetals with $POCl_3$ [14], and iodine-catalyzed cyclocondensation of 1,2-dicarbonyl compounds with *o*-phenylene diamine in DMSO or CH_3CN [15]. The quinoxaline derivatives are also synthesized by reaction of α-hydroxyl ketones with *o*-phenylene diamines in presence of HgI_2 [16], followed by oxidative cyclization of phenacyl bromides with 1,2-diamines using solid-phase synthesis [17]. Recently, the synthesis of quinoxaline derivatives was reported by reaction of 1,2 diamines with pencil bromides using catalysts like $HClO_4$:SiO_2 [18], $CuSO_4 \cdot 5H_2O$ [19], and DABCO [20]. However, many of these methods suffered from some drawbacks such as low yield, long reaction time, drastic reaction condition, and tedious work-up. Co-occurrence of several side reactions and in some cases more than one step is involved in the synthesis of compound. As a part of our research, the use of nanoparticles as a catalyst for organic synthesis, we have reported the use of Fe/ZnO for the synthesis of quinoxalines.

Recently, metal oxide-based catalytic systems have been widely used in a variety of organic reactions [21, 22]. These reactions have several disadvantages such as long reaction time, low yield, and formation of bi-products [23]. These limitations can be overcome by using metal-containing metal oxide: X-Meng et.al [24] have reported catalytic oxidation by molecular oxygen catalyzed Ni–TiO_2, a similar catalyst to SO_4/ZrO_2 [25], Ru/SnO_2 [26], Ag/SiO_2[27], Au/SiO_2 [28], etc., which has been used for oxidation reaction.

With keeping all these things in our mind, we report the preparation of an efficient and recyclable 5 % Fe/ZnO nanocrystalline catalyst by a hydrothermal method for the synthesis of quinoxaline derivatives from phenacyl bromides and 1,2-diamines. In this, Fe gives redox reaction between phenacyl bromide and 1,2-diamines by the support of ZnO. The present study also includes the effect of metal-containing metal oxide (Fe/Co/Cu containing ZnO) on the cyclization of quinoxaline in comparison with ZnO nanocrystallite. The metal-containing ZnO and nanocrystalline ZnO catalyst has gained more importance due to high thermal stability, large surface area, easy recovery, good ability to perform organic reactions at lower temperatures, and enviro-economic factors [29]. It has received more attention due to its non-toxic and ecofriendly nature in performing organic reactions [30–32]. In addition, Nano ZnO is an ecofriendly material which is non-toxic for human bodies and a widely used antibacterial agent in biomedical applications [33, 34].

Experimental

All chemicals were purchased from Aldrich Chemical and were used without purification. All yields refer to isolated products after purification using column chromatography. Column chromatography was performed on silica gel (120–240 mesh) supplied by Acme Chemical. ^{1}H and ^{13}C-NMR spectra were recorded on Varian Mercury XL-300 and Bruker spectrometer instruments using

TMS as an internal standard and $CDCl_3$, DMSO-d_6 as a solvent. Infrared spectra were taken on a Shimadzu FTIR-408 in KBr. The high resolution mass spectra were recorded on a Bruker Daltonics mass spectrometer. The XRD patterns were acquired on a multi-purpose X-ray diffractometer (Philips-1710 diffractometer Cukα, λ: 1.5406 A°) at a scan rate of 0.17° 2θ s^{-1}. The nanosize and morphology of the Fe/ZnO nanoparticles were observed under Scanning Electron Micrography (JEOL JEM-6360A model) equipped with JEOL JEC-560 auto carbon coater and TEM with SAED (CM-200, Philips microscope).

Preparation of 5 % Fe/ZnO

The nanocrystalline ZnO was synthesized by the hydrothermal method using a complexing agent like resorcinol (1.3 mol) and $ZnCl_2$ (1 mol) in methanol (20 ml) at 150 °C. The complex formed was filtered, dried, and calcined at 400 °C. The product thus obtained was used for preparation of 5 % Fe/ZnO.

An appropriate amount of synthesized nanocrystalline ZnO was mixed with 5 % $FeCl_3$ solution along with buffer solution. A buffer solution (pH = 9.6) was prepared by dissolving appropriate amounts of sodium hydroxide and sodium bicarbonate in distilled water. The slurry obtained was stirred and transferred into a steel-lined autoclave kept in an oven at 100 °C for 24 h. The precipitate obtained was filtered, washed with deionized water, and dried at 100 °C for 12 h. The sample was directly placed in the furnace for calcination at 600 °C for 3 h. The product was characterized by XRD, SEM, EDAX, TEM, and SAED techniques.

Catalytic reaction

In a typical run, 1,2-diamines (1.1 mol), phenacyl bromides (1.3 mol), and Fe/ZnO (0.3 mol) nanoparticles were allowed to react in methanol at room temperature for 25 min. The reaction was monitored by TLC using ethyl acetate–hexane (3:7 v/v) as the solvent system. After the completion of the reaction, the reaction mixture was directly filtered and washed with methanol. Filtrate was collected and evaporated under reduced pressure to afford the crude product. The products obtained were purified by recrystallization method using ethanol/water, followed by column chromatography on silica gel with *n*-hexane:ethyl acetate (70:30) as an eluent to afford the pure product. All products were characterized by IR, ^{1}H, and ^{13}C-NMR and mass spectrometry. The recovered catalyst was dried and reused further in successive reactions.

Spectral data of selected and unknown compounds

2-(4-chlorophenyl)quinoxaline

IR (KBr) *v*: 3,039, 1,609, 829, 748 cm^{-1}, ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.40 (*s*, 1H), 8.37 (*d*, J = 8.4 Hz, 2H), 8.3–8.11 (*m*, 2H), 7.90–7.85 (*m*, 2H), 7.65 (*d*,

$J = 8.7$ Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 150.56, 142.86, 142.18, 141.63, 136.55, 135.15, 130.46, 129.76, 129.56, 129.38, 129.13, 128.75. EA calculated: C, 69.86; H, 3.77; N, 11.64; Found C, 69.07; H, 4.21; N, 11.97.

2-(3-fluoro-4-methoxyphenyl)quinoxaline

IR (KBr) *v*: 3,090, 2,364, 1,620, 813, 763 cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (*s*, 1H), 8.12–8.08 (*m*, 2H), 7.78 (*d*, $J = 8.2$ Hz, 1H), 7.76 (*d*, $J = 8.2$ Hz, 1H), 7.14–7.10 (*m*, 2H), 3.98 (*s*, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): [154.38, 151.11, 150.13, 149.61 (1*c*, *d*, $J = 245$ Hz)], 142.62, 142.12, 141.35, 130.35, 129.79, 129.40, 129.04, 123.55, 115.21, 114.95, 113.40, 56.28. EA Calculated: C, 70.54; H, 4.17; N, 11.22; Found: C, 70.97; H, 4.41; N, 11.03.

2-(3,5-bis(trifluoromethyl)phenyl)quinoxaline

IR (KBr) *v*: 3,093, 2,341.58, 1,624, 902, 763 cm^{-1}, ^{1}H NMR (400 MHz $CDCl_3$): δ 9.38 (*s*, 1H), 8.68 (*s*, 2H), 8.21–8.16 (*m*, 2H), 8.02 (*s*, 1H), 7.87–7.81 (*m*, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): [132.79, 132.46, 132.13, 131.79 (2*c*, *q*, $J = 33$ Hz)], [126.90, 124.23, 121.52, 118.81 (2*c*, *q*, $J = 271$ Hz)], 148.07, 141.9, 141.77, 138.48, 130.67, 130.41, 129.48, 128.99. EA Calculated: C, 56.15; H, 2.36; N, 8.19; Found C, 55.83; H, 2.74; N, 8.56.

2,3-dihydro-5-(4-nitrophenyl)pyrazine

IR (KBr) *v*: 3,058, 1,590, 1,364, ^{1}H NMR (300 MHz, $CDCl_3$): 8.67 (*s*, 1H), 7.89 (2H, *d*, $J = 8.2$ Hz), 7.58 (2H, *d*, $J = 8.2$ Hz), 3.62–3.48 (*m*, 2H), 3.22–2.90 (*m*, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 162.42, 157.59, 150.80, 147.65, 134.13, 128.90, 120.10, 54.34, 53.18. EA Calculated: C, 57.25; H, 3.14; N, 12.84; Found: C, 57.49; H, 3.36; N, 12.52.

Results and discussion

In this study, we have prepared 5 % Fe/ZnO nanocatalyst by a hydrothermal method using synthesized ZnO, $FeCl_3$, deionized water, and NaOH. The XRD patterns of 5 % Fe/ZnO are shown in Fig. 1. The diffraction peaks at scattering angles (2θ) of 29.0117, 31.8, 34.4, 36.2, 47.5, 56.6, 62.9, and 67.9° correspond to the reflection from 002, 100, 102, 101, 102, 110, 103, and 112 crystal planes, respectively, which matches with standard JCPDS data (Card No. 36-1451). The XRD pattern of 5 % Fe/ZnO is identical to the hexagonal phase with wurtize structure having space group (C6 V = $P\bar{6}_3$ mc). The XRD pattern of 5 % Fe/ZnO sample almost coincides with that of pure ZnO showing no diffraction peaks due to Fe_2O_3, and also indicates that Fe may be incorporated in ZnO. The value of 60–70 nm was calculated from XRD data for the average diameter of this nanocrystalline 5 % Fe/ZnO using Scherrer's equation.

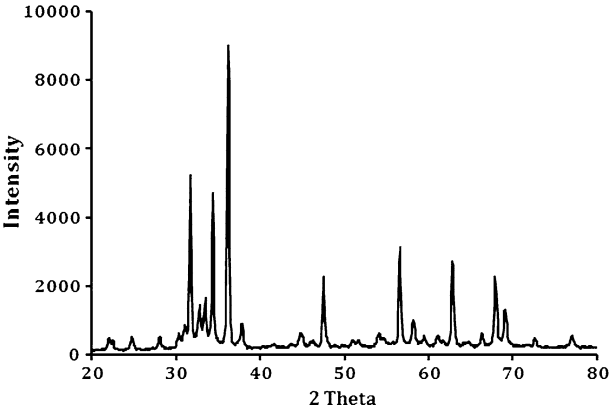


Fig. 1 XRD pattern of 5 % Fe/ZnO

The SEM images of 5 % Fe/ZnO powders are represented in Fig. 2a. The shapes of the particles are quite similar to each other and are almost spherical. The SEM images also reveal that the 5 % Fe/ZnO powder particles are agglomerates. The agglomeration may result from the chemical treatment conditions. Figure 2b shows EDAX analysis of 5 % Fe/ZnO, which indicates that 4.7 % of Fe is present in the system. The loss in Fe content may be due to leaching out of unbound Fe by washing.

The TEM image along with the selected area of the diffraction pattern (SAED) (Fig. 3a, b) recorded for the sample corresponding to 5 % Fe/ZnO. TEM reveals that the nanoparticles are hexagonal with several spherical-shaped crystallites. The dark spot in the TEM micrograph can be alluded to synthesized 5 % Fe/ZnO nanoparticles as the SAED pattern associated with such spots reveals the occurrence of wurtize 5 % Fe/ZnO in total agreement with the XRD data. The average size of the 5 % Fe/ZnO nanocrystallites was found to be 62.3 nm.

Catalytic results

In order to get effective results, the reaction conditions were optimized. For this purpose, *o*-phenylene diamine and *p*-chloro phenacyl bromide was used as the model substrate for the synthesis of quinoxaline (Scheme 1). The probable mechanism for synthesis of quinoxaline is shown in Scheme 2. The process conditions were optimized in terms of the following reaction variables.

Initially, a blank reaction was carried out using *p*-chloro phenacyl bromide and *o*-phenylene diamine in methanol at room temperature which resulted in no quinoxaline product even after 5 h at room temperature. The same reaction carried out using a catalytic amount of 5 % Fe/ZnO afforded the desired quinoxaline with 94 % yield in 25 min.

To check the effectiveness of Fe/ZnO with different catalysts, we tried synthesized ZnO, Fe/ZnO, Co/ZnO [35], and Cu/ZnO [36] for the cyclization

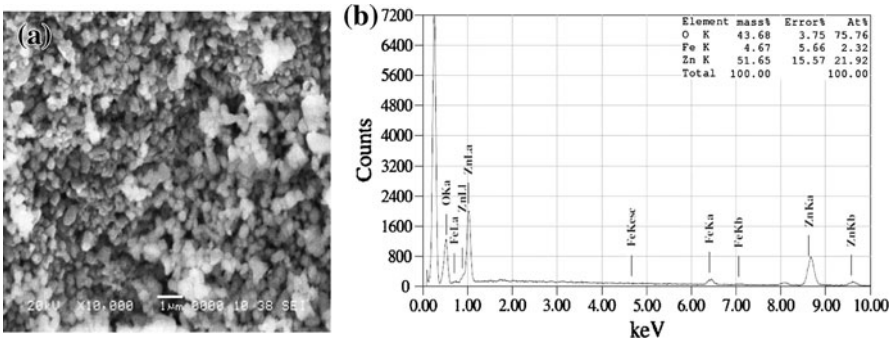


Fig. 2 SEM and EDAX of 5 % Fe/ZnO

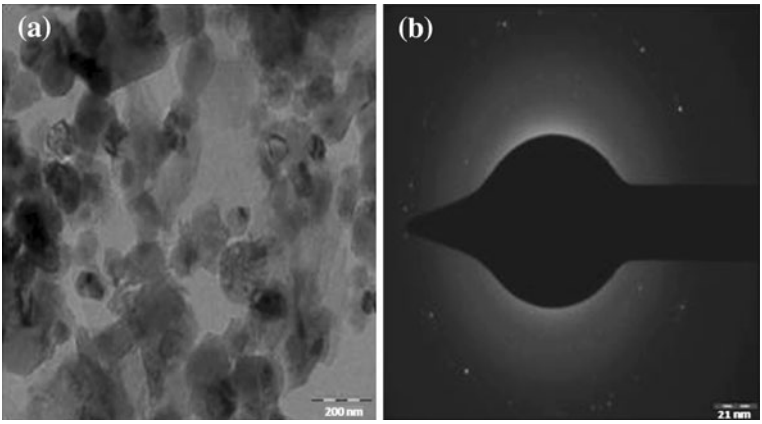
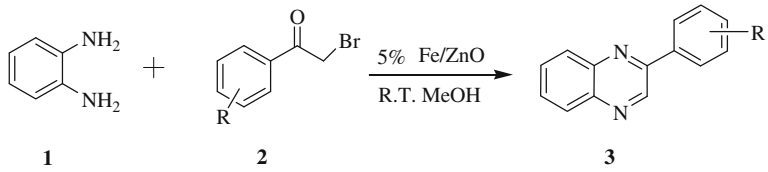


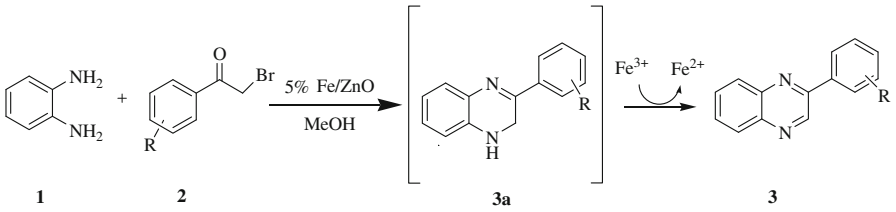
Fig. 3 TEM and SAED of 5 % Fe/ZnO



Scheme 1 Synthesis of quinoxaline

reaction of *o*-phenylene diamine and *p*-chloro phenacyl bromide. ZnO gave poor yield while Cu and Co/ZnO gave good yield, but required more time as compared to Fe/ZnO, also 5 % Fe/ZnO gave good yield with less time compared to 3 and 10 % Fe/ZnO. The results are shown in Table 1.

With increasing Fe loading from 0 to 10 %, cyclization substantially increases and reaches the maximum (94 %) at Fe content of 5 %. Further increasing Fe content, however, lowers the cyclization rate. As evidenced by XRD, Fe species loadings are lower than 10 %, whereas high Fe content results in microcrystalline



Scheme 2 Probable mechanism of quinoxaline

Table 1 Effect of different dopant on reaction time and yield

Entry	Catalyst	Time (min)	Yield[a]
1.	ZnO	120	57
2.	3 % Fe/ZnO	37	79
3.	5 % Fe/ZnO	25	94
4.	10 % Fe/ZnO	30	89
5.	Cu/ZnO	50	91
6.	Co/ZnO	65	86

[a] Isolated yield

phase Fe located outside the internal channels, resulting in a remarkably poor catalytic activity. Therefore, it is likely that a moderate incorporation of Fe results in higher catalytic activity. Thus, it is obvious from our studies that 5 % Fe/ZnO was superior in the cyclization reaction with good yield in a short time.

To optimize the amount of catalyst required for the cyclization, we tried various mol equivalents of the catalyst compared to the quantity of the *o*-phenylene diamine (Table 2). It was found that, when the reaction was carried out with 0.3 mol equivalents, cyclization was 94 %.

The cyclization reaction was carried out in different solvents such as DMF, MeOH, EtOH, CH_3CN, and CH_2Cl_2, and the results clearly showed that methanol was found to be the best choice, as shown in Table 3. Treatment of substituted phenacyl bromides with *o*-phenylene diamine or ethylene diamine in methanol with 5 % Fe incorporating ZnO (0.3 mol) at room temperature afforded quinoxalines with excellent yield, while the absence of the catalyst under similar conditions led to the formation of DHQ (**3a**). The generality of the cyclization reaction of *o*-phenylene diamine was checked by treating with a wide range of substituted phenacyl bromides, and the results obtained are shown in Table 4.

However, with ethylene diamine, similar reactions furnished DHPs and in only moderate yields. The method has also been applied for the preparation of dihydropyrazine using phenacyl bromide and 1,2-diamine. It is worth mentioning that the present method provides for the synthesis of some new furnished quinoxalines (Table 4, entries 7, 8 and 11) which have not been previously synthesized.

The effect of electron-donating and electron-withdrawing substituents on the aromatic ring of phenacyl bromide on the rate of reaction was investigated.

Table 2 Effect of mole percentage of 5 % Fe/ZnO

Entry	(mol) of Fe/ZnO	Time (min)	Yield[a]
1.	0.1 mol	120	77
2.	0.2 mol	45	89
3.	0.3 mol	25	94
4.	0.6 mol	25	87

[a] Isolated yield

Table 3 Effect of solvent for quinoxaline formation using 5 % Fe/ZnO

Entry	Solvent	Time	Yield[a]
1.	MeOH	25	94
2.	DMF	45	86
3.	CH_3CN	40	89
4.	EtOH	25	91
5.	CH_2Cl_2	60	69

[a] Isolated yield

As Table 4 demonstrates, electron-donating groups and electron-withdrawing substituents influence the reaction, with the electron-donating groups furnishing the corresponding quinoxaline in high yield with less time (Table 4, entries 1–3, 5 and 7), whereas the electron-withdrawing substituents needed a longer reaction time with low yield (Table 4, entries 4 and 11). Moreover, it has been observed that the electronic properties of the aromatic ring of phenacyl bromide have some effect on the yield and reaction times.

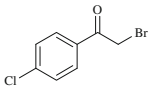
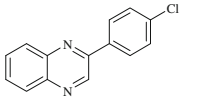
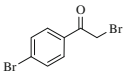
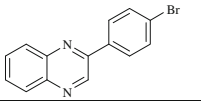
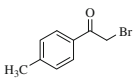
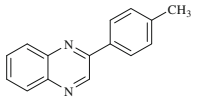
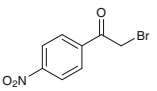
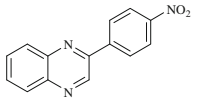
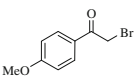
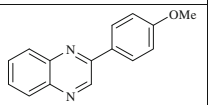
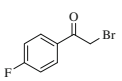
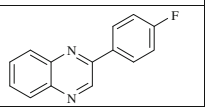
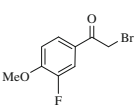
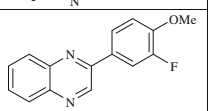
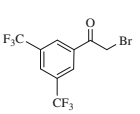
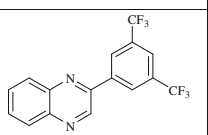
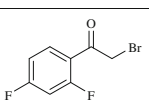
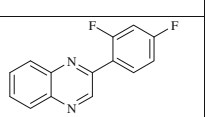
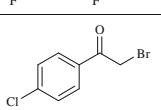
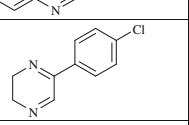
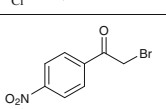
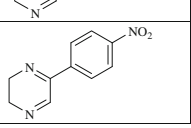
In order to study the possibility of reusability, the catalyst was filtered, washed with methanol, and calcined at 200 °C in oven for 2 h. The reusability of the catalyst was checked for several successive runs under identical reaction conditions. The catalyst was found to be stable and reusable even after five cycles without appreciable loss in activity, which is shown in Table 5.

In order to prove that the reaction is heterogeneous, a standard leaching experiment was conducted. The catalyst was filtered at the reaction temperature and the reaction was allowed to proceed without a catalyst. There was no change in yield even after 12 h reflux, indicating that no homogeneous catalyst was involved.

Conclusion

In conclusion, the present paper describes a new, efficient, and eco-friendly catalyst for the synthesis of quinoxalines. The 5 % Fe/ZnO catalyst exhibits excellent catalytic activity for the condensation of various aromatic phenacyl bromides and *o*-phenylene diamine. Most importantly, this catalyst facilitates the reaction at room temperature providing solid supports in the reaction, enhances the reaction rate, and

Table 4 Synthesis of quinoxaline in the presence of 5 % Fe/ZnO nanoparticles

Entry	Phenacyl bromide	1,2 diamine	Time	Product	Isolated yield [a,b]	Ref.
1			25		94	18
2			20		91	18
3			35		93	18
4			15		86	20
5			35		94	18
6			20`		92	12
7			15		96	--
8			15		91	--
9			25		87	16
10			60		87	18
11			30		83	--

[a] Isolated yield

[b] All the products were characterized by ^{1}H, ^{13}C NMR and MS spectral data and were compared with the reference compounds. The products were characterized by comparison of their spectroscopic and physical data with reference samples

Table 5 Results of the reaction run in the presence of recycled catalyst

Entry	Reaction run	Time	Yield[a]
1.	1	25	94
2.	2	25	94
3.	3	25	92
4.	4	25	93
5.	5	25	93

[a] Isolated yield

thereby the excellent yields of the products. Therefore, we concluded that the 5 % Fe/ZnO is the best catalyst for the synthesis of quinoxaline.

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