Ni@Zeolite-Y Nano-Porous: Preparation and Application as a High Efficient Catalyst for Facile Synthesis of Quinoxaline, Pyridopyrazine, and Indoloquinoxaline Derivatives

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ABSTRACT: *In this research, by a simple and modified method, nanoporous of Ni(II) ion loaded Y-type zeolite (NNZ) was designed and applied as a novel highly efficient catalyst for the synthesis of quinoxalines, pyrido[2,3-b]pyrazines, and indolo[2,3-b]quinoxalines* ***3a-s****. These heterocycles were obtained through a one-pot condensation reaction of aryl-1,2-diamines with 1,2-diketones or the isatin in the presence of the catalytic amount of Ni@zeolite-Y in ethanol or acetic acid at room temperature giving good to excellent yield. The structure of entitled catalyst was identified with FT-IR spectroscopy, Energy Dispersive X-ray (EDX), Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) analysis. This method has some advantages such as the use of inexpensive, safety, stable and recyclable catalyst, high yields, short reaction times, and easy isolation of the product. It can be claimed that this approach in simplicity covers the goals of green chemistry.*

KEYWORDS: *Synthesis; Ni@zeolite-Y; Nano-catalyst; o-arylenediamines; Isatin; Quinoxaline, Pyridopyrazine; Indoloquinoxaline*

INTRODUCTION

Quinoxaline derivatives, although known compounds are old, due to the growing use in dyes, pharmaceuticals, and electrical/photochemical materials, they still have great importance among chemical and industrial researchers [1-9]. One of the interesting application of these derivatives is the presence of quinoxaline ring moiety in the structure of drugs such as Echinomycin, Levomycin, and Actinoleutin [10,11]. It is also known that if an active nucleus is linked to another, the resulting molecule may possess greater potential for biological activity. Of these compounds, the pyridopyrazines and indoloquinoxaline derivatives an important class of fused heterocyclic compounds, have attracted much synthetic attention for their wide range of pharmacological and therapeutic activities [12-19].

Hitherto, in addition to traditional methods, the several procedures have been reported to synthesize these compounds through the condensational reaction of an aryl 1,2-diamine with a 1,2-dicarbonyl compound in refluxing or in the presence of an acid catalyst under various reaction conditions. Many catalysts such as molecular iodine [20] Ceric(IV) ammonium nitrate [21], polyaniline sulfate salt [22], Montmorillonite K-10 [23], Gallium triflate [24] $MnCl_2$ [25], $CuSO_4{\cdot}5H_2O$ [26], Zn/L-proline [27],

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Zirconium tetrachloride [28], Zeolite Y [29,30], Zirconium tetrakis (dodecyl sulfate) [31], $(NH_4)H_2PW_{12}O_{40}$ [32], Fe_3O_4@SiO_2/Schiff base complex [33], $CuCl_2$/MS 4A [34], $NbCl_5$ [35], sulfated TiO_2-P25 [36], $CrCl_2.6H_2O$ [37], SBA-15/Cu-Schiff base complex [38] and $La(AcO)_3$ [39] have been explored. Also, for the synthesis of indoloquinoxalines, pertaining to $Pd(OAc)_2$, Et_3N [40], Ce.MCM-41 [41], AcOH/reflux [42], sulfamic acid [43], benzyl triethyl ammonium chloride (BTEAC) [44], have been reported. However, each of these methodologies is having one or more disadvantages. Consequently, the introduction of new methods and/or further effort on technical improvements to overcome these limitations is still in demand.

Recently, the zeolites as solid acid heterogeneous catalysts have attracted the growing attention of many chemists and activists of the chemical industry. These microporous materials have advantages such as proper acidity, thermal stability, non-toxic, easy handling, environmentally friendly. They also have qualities such as insolubility in all organic solvents, low cost and the facile conversion into nanoscale materials. The acidity and catalytic activity of zeolite can be affiliated to Lewis and Bronsted acid sites [45]. The dehydration reaction, can decrease the number of proton sites and increase the number of Lewis acid sites. The exchange or relocation of monovalent cations with polyvalent ions also creates strong Bronsted centers using the hydrolysis phenomenon [46]. These processes can be useful for catalytic reactions such as alcohol dehydration [47], acylation [48], esterification [49], oxidation [50], desulfurization [51], epoxidation [52], methylation [53], adsorption [54] and cyclization [55,56].

Following our interest researches on the development of new methods for the synthesis of important heterocyclic rings by solid nanocatalysts [56-58], in this paper, we intend to report the design and procurement of Ni@zeolite-Y nanoporous and its application as a highly efficient and safety catalyst for the synthesis of 2,3-diaryl quinoxaline, pyrido[2,3-*b*]pyrazine, and indolo[2,3-*b*]quinoxaline derivatives *via* a one-pot condensation reaction of *o*-arylene diamines and 1,2-dicarbonyl compounds or substituted isatins in green conditions.

EXPERIMENTAL SECTION

Melting points were determined by the use of a Barnstead Electrothermal 9200 apparatus and they may be uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker spectrophotometer (300 and 500 MHz) in DMSO-d_6, with Me_4Si as an internal standard. IR spectra were acquired with a JASCO FT-IR 4200-A spectrophotometer. The mass spectra were recorded on an Agilent model 5975C VL MSD with a Triple-Axis Detector spectrometer at 70 eV. The shape, size and atom type of nano-particles were examined by SEM and EDX images recorded by Philips XL30. Nitrogen adsorption and desorption isotherms (BET analysis) were measured at -196°C by a Japan Belsorb II system after the samples were vacuum dried at 150°C overnight. The progress of reactions was routinely monitored by thin-layer chromatography on silica gel F_{254} aluminium sheets (Merck). All chemicals were used as obtained without further purification.

Preparation of nano-Ni@zeolite Y

To 2.0 g NaY zeolite in a 150-mL flask (obtained in our laboratory in accordance with the previously reported method [56]), was added an aqueous solution of $NiCl_2.2H_2O$ (0.01 M, 100 mL) at room temperature. The mixture was stirred for 24 h and then filtered. The resulting precipitate was washed with water until the filtrate was colorless. The Ni/zeolite-Y (0.2 g) was handled with ultrasound for 1 h to provide nano size particles. The nano-catalyst was then used without further purification.

The typical procedure for preparation of compounds (3a-s)

The 1,2-arylenediamine, **1a-c** or 2,3-diaminopyridine, **1d** (0.1 mmol) and the corresponding 1,2-diketones, **2a-d** or the isatin derivatives, **2e-g** dissolved in ethanol or acetic acid with constant stirring. Then a catalytic amount (3 or 10%, w/w) of nano Ni@zeolite–Y was added to the solution. The reaction mixture was stirred at room temperature for 5-30 minutes (Table 2). The reaction progress was monitored by TLC. After completion of the reaction, the used catalyst was collected by filtration and cold water was added to the filtrate to give the product. Then, the solid product was filtered and washed with cold ethanol/water to give the compounds **3a-s**. In some cases for further purifications, the crude products were purified by recrystallization from EtOH (quinoxalines and pyridopyrazine**s)** and AcOH/MeOH (indoloquinoxalin**s)**.

Spectroscopic data for selected compounds

2,3-Diphenyl quinoxaline (3a)

White solid, IR (KBr, υ_{max}): 3056 (CH), 1544, 1477 (C=N) 1440, 1345, 1218 (C=C), 1057, 977, 770, 698, 598, 539 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 8.19 (dd, J = 3.40 Hz, J = 2.90 Hz, 2H, H-Ar), 7.77 (dd, J = 3.45 Hz, J = 3.01 Hz, 2H, H-Ar), 7.53 (m, 4H, H-Ar), 7.37-7.32 (m, 6H, H-Ar) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C: 153.5, 141.2, 139.1, 129.9, 129.6, 129.3, 128.8, 128.3 ppm.

6-Methyl-2,3-diphenyl quinoxaline (3b)

White solid, IR (KBr, υ_{max}): 2916 (CH), 1620 (C=N), 1345 (C=C), 1058, 808, 700 cm-1; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 8.09 (d, J = 8.40 Hz, 1H, HAr), 7.96 (s, 1H, H-Ar), 7.62 (q, J_1 = 1.80 Hz, J_2 = 6.90 Hz, 1H, H-Ar), 7.53-7.51 (m, 4H, H-Ar), 7.35-7.30 (m, 6H, H-Ar), 2.62 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 153.3, 152.5, 141.3, 140.4, 139.7, 139.2, 132.3, 129.8, 129.8, 128.7, 128.7, 128.6, 128.2, 128.0, 21.9 ppm.

6-Nitro-2,3-dipenylquinoxaline (3c)

Yellow solid. IR (KBr, υ_{max}): 1659 (C=N), 1593, 1315 (NO_2), 1450, 1211 (C=C), 876, 718, 643 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 9.08 (d, J = 2.47 Hz, 1H, H-Ar), 8.51 (q, J_1 = 2.49 Hz, J_2 = 6.65 Hz, 1H, H-Ar), 8.30 (d, J = 9.14 Hz, 1H, H-Ar), 7.57-7.54 (m, 4H, H-Ar), 7.44-7.36 (m, 6H, H-Ar) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ_C: 156.4, 155.7, 147.9, 143.5, 139.8, 138.3, 138.0, 130.8, 130.0, 129.8, 129.7, 129.5, 128.6, 125.3, 123.4 ppm.

2,3-Diphenyl pyrido[2,3-*b*]pyrazine (3d)

Yellow solid. IR (KBr, υ_{max}): 3056 (C-H), 1544 (C=N), 1430, 1384, 1332 (C=C), 1068, 1019, 780, 697 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ_H: 9.15 (d, J = 3.52 Hz, 1H, H-Ar), 8.57 (dd, J = 1.32, 6.90 Hz, 1H, H-Ar), 7.87 (q, J = 4.14 Hz, 1H, H-Ar), 7.49-7.31 (m, 10H, H-Ar) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ_C: 156.5, 155.3, 154.9, 150.0, 139.1, 138.7, 136.5, 130.6, 130.6, 130.0, 129.9, 128.9, 126.8 ppm.

Dibenzo[*f*,*h*]pyrido[2,3-*b*]benzopyrazine (3h)

Yellow solid (partial to brown), IR (KBr, υ_{max}): 1600, 1497 (C=N), 1447, 1359, 1199 (C=C), 1023, 757, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 9.56 (d, J = 8.10 Hz, 1H, H-Ar), 9.36-9.31 (t br, 2H, H-Ar), 8.70 (d, J = 8.40 Hz, 1H, H-Ar), 8.58 (d, J = 8.10 Hz, 2H, H-Ar), 7.83-7.72 (m, 5H, H-Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 154.7, 150.0, 145.2, 143.9, 138.4, 137.4, 132.6, 132.4, 131.2, 131.0, 129.8, 129.6, 128.2, 128.0, 127.5, 126.6, 125.0, 123.1, 122.9 ppm.

Acenaphtho[1,2-*b*]pyrido[2,3-*e*]pyrazine (3l)

White solid (partial to Yellow), IR (KBr, υ_{max}): 3050 (C-H), 1613, 1489 (C=N), 1435, 1375, 1298, 1205 (C=C), 1097, 1034, 827, 771 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 9.13 (d, J = 4.20 Hz, 1H, H-Ar), 8.57 (dd br, 2H, H-Ar), 8.41 (d, J = 6.90 Hz, 1H, H-Ar), 8.16 (dd, J = 2.40, 7.50 Hz, 2H, H-Ar), 7.90-7.83 (m, 2H, H-Ar), 7.74-7.69 (m, 1H, H-Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 157.3, 155.0, 152.4, 150.5, 138.3, 137.3, 136.5, 131.2, 131.0, 130.2, 130.1, 129.8, 129.0, 128.6, 124.2, 123.3, 122.4 ppm.

2,3-Bis-(4-methoxy phenyl)pyrido[2,3-*b*]pyrazine (3m)

Yellow solid, IR (KBr, υ_{max}): 2933 (C-H), 1605, 1513 (C=N), 1447, 1384 (C=C), 1251, 1175 (C-O), 1023, 833 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H: 9.12 (dd, J = 1.80, 4.20 Hz, 1H, H-Ar), 8.47 (dd, J = 1.80, 6.60 Hz, 1H, H-Ar), 7.68-7.62 (m, 3H, H-Ar), 7.55 (d, J = 8.40 Hz, 2H, H-Ar), 6.91-6.85 (m, 4H, H-Ar), 3.84 (d, 6H, $2CH_3$), ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 160.7, 155.7, 154.2, 153.5, 149.8, 137.8, 135.8, 131.8, 131.2, 131.1, 130.7, 124.7, 113.9, 113.6, 55.35, 55.30 ppm.

6*H*-Indolo[2,3-*b*]quinoxaline (3n)

Yellow solid, IR (KBr, υ_{max}): 3420 (NH), 1650, 1617, 1338 (C=N, C=C), 745, 669 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ_H: 12.04 (s, 1H, NH), 8.36 (d, J = 7.72 Hz, 1H, H-Ar), 8.26 (d, J = 8.20 Hz, 1H, H-Ar), 8.08 (d, J = 8.14 Hz, 1H, H-Ar), 7.82–7.68 (m, 3H, H-Ar), 7.60 (d, J = 8.04 Hz, 1H, H-Ar), 7.39 (t, J = 7.40 Hz, 1H, H-Ar) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 146.2, 144.4, 140.6, 139.0, 131.7, 129.5, 129.2, 127.9, 126.4, 122.7, 112.4 ppm.

2-Nitro-6*H*-indolo[2,3-*b*]quinoxaline (3o)

Yellow solid, IR (KBr, υ_{max}): 3435 (NH), 1640, 1594, 1470, 1296 (C=N, C=C), 1522, 1310 (NO_2), 1159, 810, 748 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ_H: 10.93 (s, 1H, NH), 7.96 (s, 1H, H-Ar), 7.64 (d, J = 5.72 Hz, 1H, H-Ar), 7.37 (d, J = 5.94 Hz, 1H, H-Ar), 6.90–6.73 (m, 4H, H-Ar) ppm; MS (m/z, %): 264.1 (M^+, 20), 254.1 (100), 208.1 (65), 181.1 (18), 121.1 (20), 118.1 (22), 90.1 (18).

9-Nitro-6*H*-indolo[2,3-*b*]quinoxaline (3q)

Yellow solid, IR (KBr, υ_{max}): 3426 (NH), 1712, 1655, 1271 (C=N, C=C), 1617, 1445 (NO_2), 1113, 749 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ_H: 12.57 (br, 1H, NH), 9.38 (s, 1H, H-Ar), 8.30–7.32 (m br, 6H, H-Ar) ppm; MS (m/z, %): 264.0 (M^+, 22), 254.1 (80), 208.1 (100), 181.1 (45), 118.1 (18), 90.1 (50).

7-Nitro-10*H*-pyrido[3',2':5,6]pyrazino[2,3-*b*]indole (3r)

Red solid, IR (KBr, υ_{max}): 3433, 3280 (NH), 1672, 1614, 1482 1265 (C=N, C=C), 1575, 1340 (NO_2), 1161, 1114, 834, 798, 769, 746, 571 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ_H: 12.75 (br, 1H, NH, the NH proton disappeared on D_2O addition), 9.63 (d, J = 2.52 Hz, 1H, H-Ar), 8.54–8.46 (m br, 2H, H-Ar), 9.63 (dd, J_1 = 2.73 Hz, J_2 = 6.54 Hz, 1H, H-Ar), 7.74 (dd, J_1 = 1.49 Hz, J_2 = 6.64 Hz, 1H, H-Ar), 7.58 (q, J = 4.47 Hz, 1H, H-Ar) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 113.8, 116.0 (2C), 123.7, 125.1, 126.8, 127.6, 129.3, 134.9 (2C), 145.8, 154.3, 155.1 ppm.

RESULTS AND DISCUSSION

First, using the general procedure adapted with our previous studies, Ni@zeolite-Y was synthesized in our laboratory [52,57]. The primary production of Ni@zeolite-Y was under ultrasound to obtain nano-size. This nano-material was analyzed using different techniques which were synergistic and verified the synthesis of Ni@zeolite-Y (NNZ) nano-porous. The FTIR spectrum of zeolite and Ni-doped zeolite is depicted in Fig. 1. that showed, the broad peak in 3418 cm^{-1} region may be attributed to the hydroxyl stretching of hydrogen bonded internal silanol groups and O-H stretching of water, while the peak at 1634 cm^{-1} corresponds to of bending mode of O-H group of water. Besides those, the peaks around 1017 to 722 cm^{-1} are related to the symmetric and asymmetric stretching vibrations of the Si–O–Si groups, respectively. The displacement of IR bands to lower frequencies (red-shift) in the Ni@zeolite-Y spectrum, as compared with zeolite-NaY, confirms the exchange of a number of Ni^{2+} (heavier cation) with Na cation [59]. The comparison of these two IR spectra (the band at 575 and 578 cm^{-1}) also shows the structure of the final nano-porous remains preserved, respectively [60].

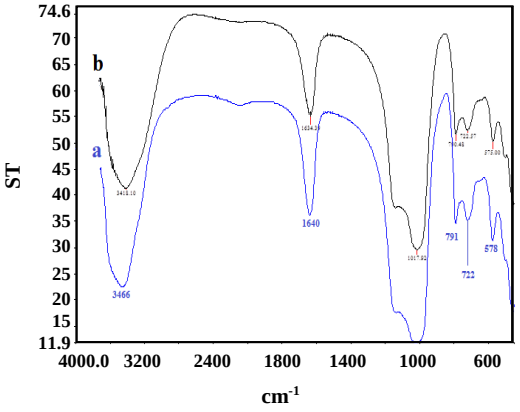


Fig. 1: The FT-IR spectrum (a) zeolite-Y and (b) Ni@zeolite-Y nano-porous.

The SEM image of the NNZ which provide valuable information about the particle size and morphology of materials is shown in (Fig. 2, a). The particles size was mainly about 54-119 nm. In the Energy Dispersive X-ray (EDX), Peak appeared in the region of 7.5 eV confirmed the presence of nickel metal deposited on zeolite, respectively (Fig. 2, b).

Atomic absorption spectroscopy was also carried out to determine the concentration of Ni(II) in the immobilized zeolite Y which was 3.56 mmol/g (21%). Nitrogen adsorption/desorption isotherms of the zeolite-Y and Ni(II)@zeolite-Y samples are shown in Fig. 2. Zeolite -Y exhibits type I isotherms whereas Ni@zeolite-Y display type IV isotherms with a very small H_1 hysteresis loop in the range of 0.5–0.9 p/p^0 according to the IUPAC classification. These isotherms demonstrate maintenance of the microporous structure of zeolite-Y after insertion of nickel(II) ions.

The values of the structural parameters obtained from the BET analysis are summarized in Table 1. The glance at this table demonstrates that the surface area, pore volume and maximum pore volume of Ni(II)/zeolite-Y decreased with cation exchange of nickel (II) ion inside the micro pores of zeolite-Y.

After proving the structure of the prepared nanoporous (NNZ), its catalytic activity was investigated in the synthesis of quinoxaline and pyridopyrazine derivatives *via* a condensation reaction between aryl-1,2-diamine or pyridine-2,3-diamine with 1,2-diketones or the isatin.

In the following, to obtain the optimal method conditions, the effect of solvent and the amount of

Table 1: Porosimetery values for zeolite-Y and functionalized its

Material	Surface area (m^2/g)	Pore volume (cm^3/g)	Maximum pore volume (cm^3/g)[a]
Zeolite -Y	619.66	0.0667	0.3092
Ni (II)@zeolite-Y	270.47	0.0536	0.0089

a) At p/p° = 0.174699824 (estimated using the Horvath-Kawazoe method)

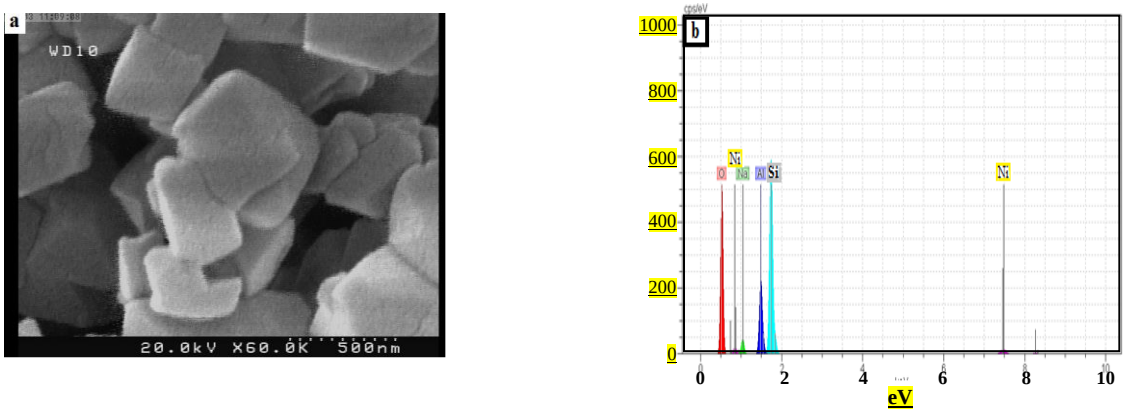


Fig. 2: SEM image (a) and EDX spectrum (b) of Ni(II)@zeolite-Y nanoparticles.

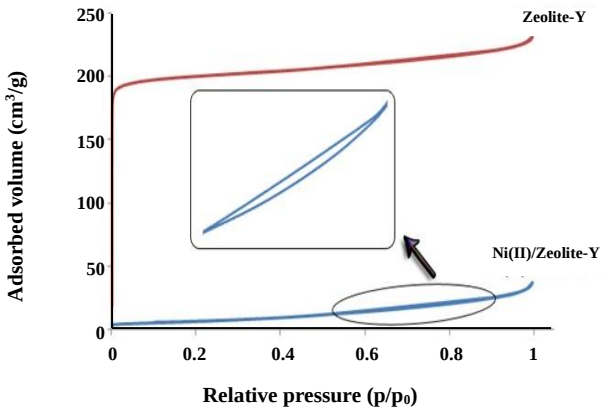


Fig. 3: N_2 adsorption/desorption isotherms of the zeolite -Y and Ni@zeolite-Y samples.

efficient catalyst on the yield of the reaction was examined. From summarized data in Tables 2, 3 and 10 W% of NNZ as the best catalyst percentage in ethanol made the highest yield (95% and 90%) in a model reaction of benzene-1,2-diamine or pyridine-2,3-diamine with benzil at ambient temperature (Table 1, entry 3 and entry 17). Also, the best yield (90%) for the model reaction of *o*-phenylenediamine and isatin at room temperature in acetic acid as the solvent with 10 W% catalysts was obtained (Table 1, entry 13). The synthetic pathway of the model reaction shown in Scheme 1.

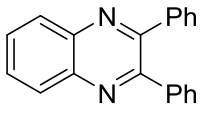
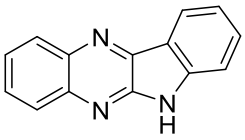
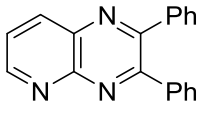
To display the scope and performance of the optimized nanocatalyzed construction of quinoxaline, pyrido[2,3-*b*]pyrazine, and indolo[2,3-*b*]quinoxaline heterocycles **3a-s**, aryl-1,2-diamines, were subjected to the one-pot reaction with the 1,2-diketones or the isatin (Scheme 2). The results are presented in Table 2.

For the investigation of the reusable property of the catalyst, it was applied in model reaction, under the same optimized conditions (Table 1, entry 3). Then the first reaction filtrated catalyst, recovered by refluxing in ethanol for 4h, drying at oven to 100 °C and reused in subsequent reactions with a small decreasing in activity even after the fourth run. The results are shown in Table 4. We also tested the recovered catalyst of the reaction by the atomic absorption spectroscopy (3.72 mmol/g, 22%) and no the Ni leaching to the solution was found.

The results Table 3 indicate that the presence of electron-withdrawing ($-NO_2$) substituent on the phenyl ring diamine, decreased the reaction yield relatively and substituted electron-donating (CH_3) was the contrary. Except for **3r**, other compounds **3a-q** and **3s** are known, being their physical and spectroscopic data in accordance with the reported in the literature [38, 42,43, 61-65].

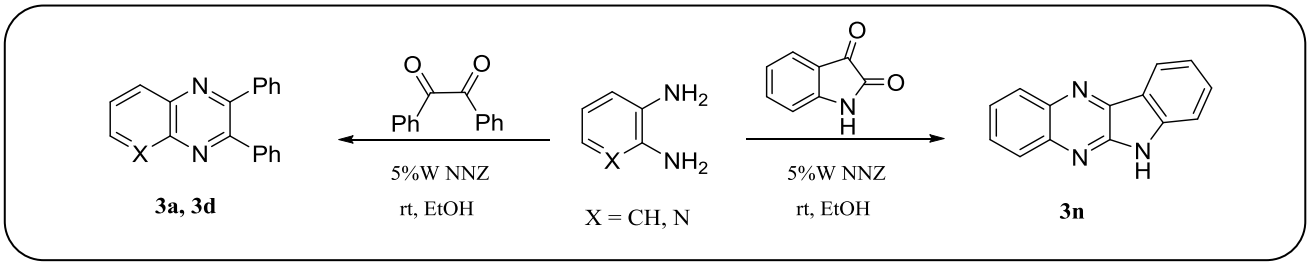
The probable reaction mechanism for the synthesis of the products **3a-m** is proposed in Scheme 3. Firstly, nano-Ni@zeolite activates the carbonyl group of the

Table 2: Results from the optimization of conditions for preparation of compounds 3a, 3d and 3n using different amounts of nano Ni@zeolite-Y as a catalyst and kind of solvents at room temperature.

Entry	Product	Solvent	Catalyst (%, *w/w*)	Time (min)	Yield(%)[a]
1	 **3a**	EtOH	5	5	95
2		EtOH	10	5	86
3		EtOH	3	5	95
4		CH_2Cl_2	3	15	65
5		MeOH	3	5	80
6		1,4-Dioxane	3	10	20
7		H_2O[b]	3	50	10
8		EtOH	0	15	35
9	 **3n**	EtOH	3	25	45
10		EtOH	5	20	52
12		CH_3COOH	5	15	69
13		CH_3COOH	10	15	90
14		CH_3COOH	15	15	72
15		1,4-Dioxane	10	20	20
16		CH_3COOH	0	30	40
17	 **3d**	EtOH	5	35	55
18		EtOH	10	25	90
19		EtOH	15	25	90
20		CH_2Cl_2	10	30	70
21		EtOH	0	15	30

[a] *Isolated yield*

[b] *The reaction was also performed under refluxing, but very little product was obtained*



Scheme 1: The optimization of conditions for the model reaction

1,2-diketone to form intermediate (A), and then the aryl-1,2-diamine as a nucleophile attack it to afford the intermediate (B) that can have followed by catalytic oxidation for forming the intermediate (C). Eventually, the under second catalytic activating and undergoing intermolecular nucleophile attack and the loss of the second water molecule, cyclization of quinoxaline, pyrido[2,3-*b*]pyrazine, and indolo[2,3-*b*]quinoxaline rings **3a-s** can be done.

Comparison of the efficiency of nano-Ni@zeolite-Y in the formation of compounds **3a**, **3d** and **3n** with those of several reported in the literature, indicates that this

Table 3: Synthesis of the quinoxaline, pyridopyrazine, and indoloquinoxalin derivatives 3a-s in the presence of 3 and/or 10 W% nano Ni@zeolite-Y as catalyst in ethanol or/and acetic acid at room temperature.

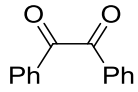
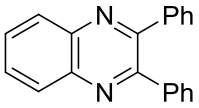
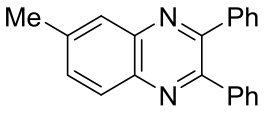
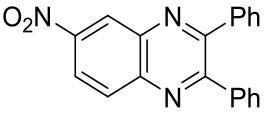
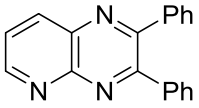
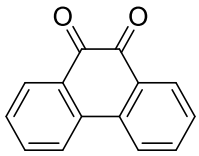
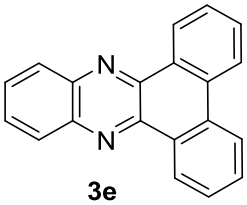
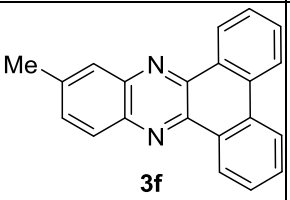
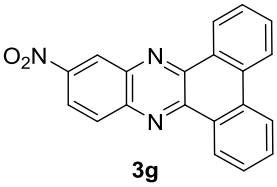
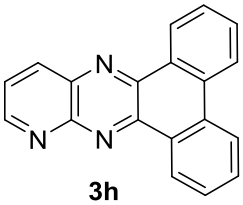
1,2-Diketone	1,2-Diamine		Product	Time (min)	M.p (°C) (Lit.)[a]	Yield (%)[b]
	X	R^1				
 **2a**	CH	H	 **3a**	5	123-125 (121-123)[62]	95
	CH	Me	 **3b**	7	121-124 (117-118)[63]	88
	CH	NO_2	 **3c**	10	185-187 (185-187)[63]	79
	N	H	 **3d**	25	137-139 (134-137)[63]	90
 **2b**	CH	H	 **3e**	5	221-223 (223-225)[62]	93
	CH	Me	 **3f**	10	219-221 (218-220)[61]	98
	CH	NO_2	 **3g**	12	259-261 (259-260)[61]	89
	N	H	 **3h**	15	215-217 (221-223)[61]	82

Table 3: Synthesis of the quinoxaline, pyridopyrazine, and indoloquinoxalin derivatives 3a-s in the presence of 3 and/or 10 W% nano Ni@zeolite-Y as catalyst in ethanol or/and acetic acid at room temperature. (Continued)

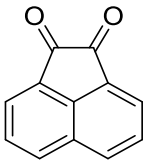
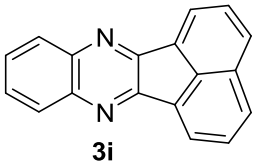
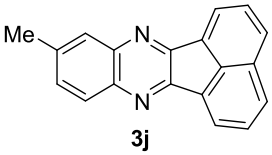
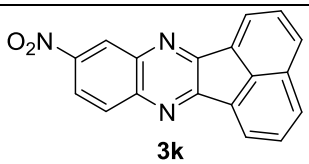
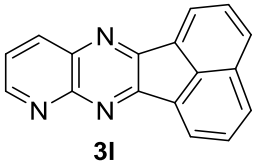
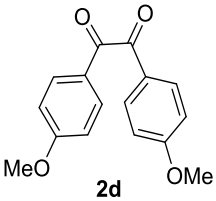
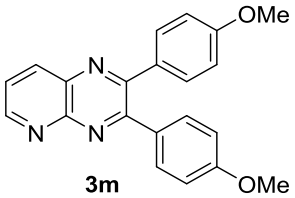
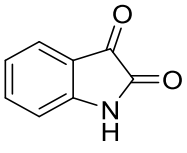
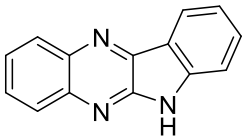
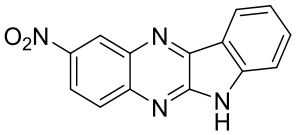
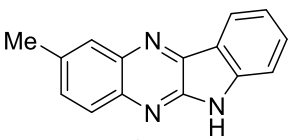
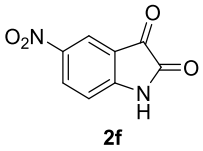
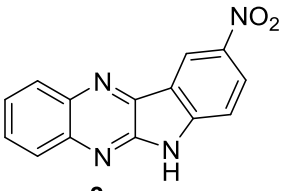
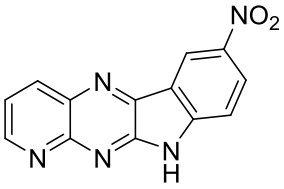
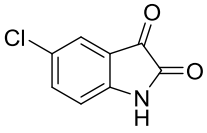
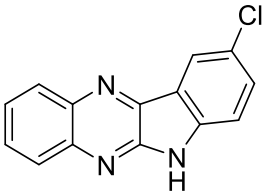
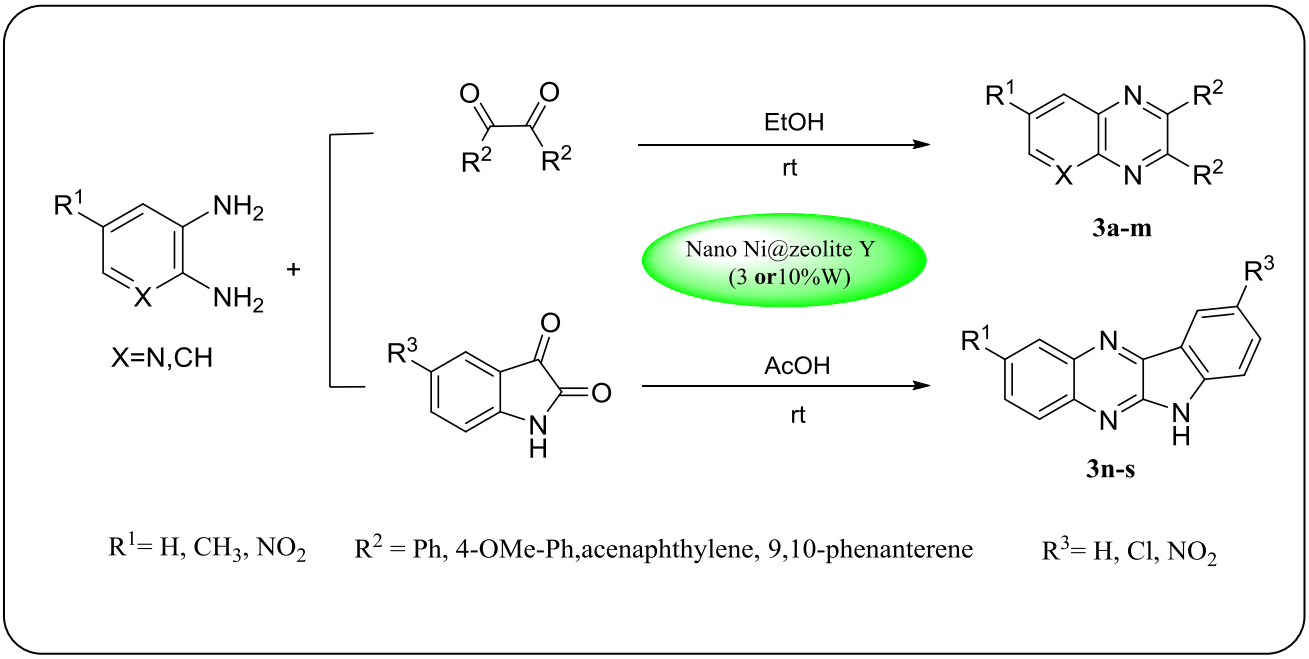
1,2-Diketone	1,2-Diamine		Product	Time (min)	M.p (°C) (Lit.)[a]	Yield (%)[b]
 **2c**	CH	H	 **3i**	7	236-238 (238-240)[62]	77
	CH	Me	 **3j**	8	229-231 (228-229)[61]	87
	CH	NO_2	 **3k**	5	318-321 (321-323)[61]	85
	N	H	 **3l**	10	227-229 (229-231)[61]	92
 **2d**	N	H	 **3m**	30	130-132 (131-134)[61]	79
 **2e**	CH	H	 **3n**	15	289-291 (288-289)[42]	90
	CH	NO_2	 **3o**	15	244-246 (363-365)[64]	88
	CH	Me	 **3p**	15	262-264 (260-262)[65]	91

Table 3: Synthesis of the quinoxaline, pyridopyrazine, and indoloquinoxalin derivatives 3a-s in the presence of 3 and/or 10 W% nano Ni@zeolite-Y as catalyst in ethanol or/and acetic acid at room temperature. (Continued)

1,2-Diketone	1,2-Diamine		Product	Time (min)	M.p (°C) (Lit.)[a]	Yield (%)[b]
 **2f**	CH	H	 **3q**	10	353-355 (>320)[42]	82
	N	H	 **3r**	25	>350	78
 **2g**	CH	H	 **3s**	7	286-288 (222-224)[43]	75

a) Melting points in parentheses are reported in the literature [42,43, 61-65]. b) Isolated yield.

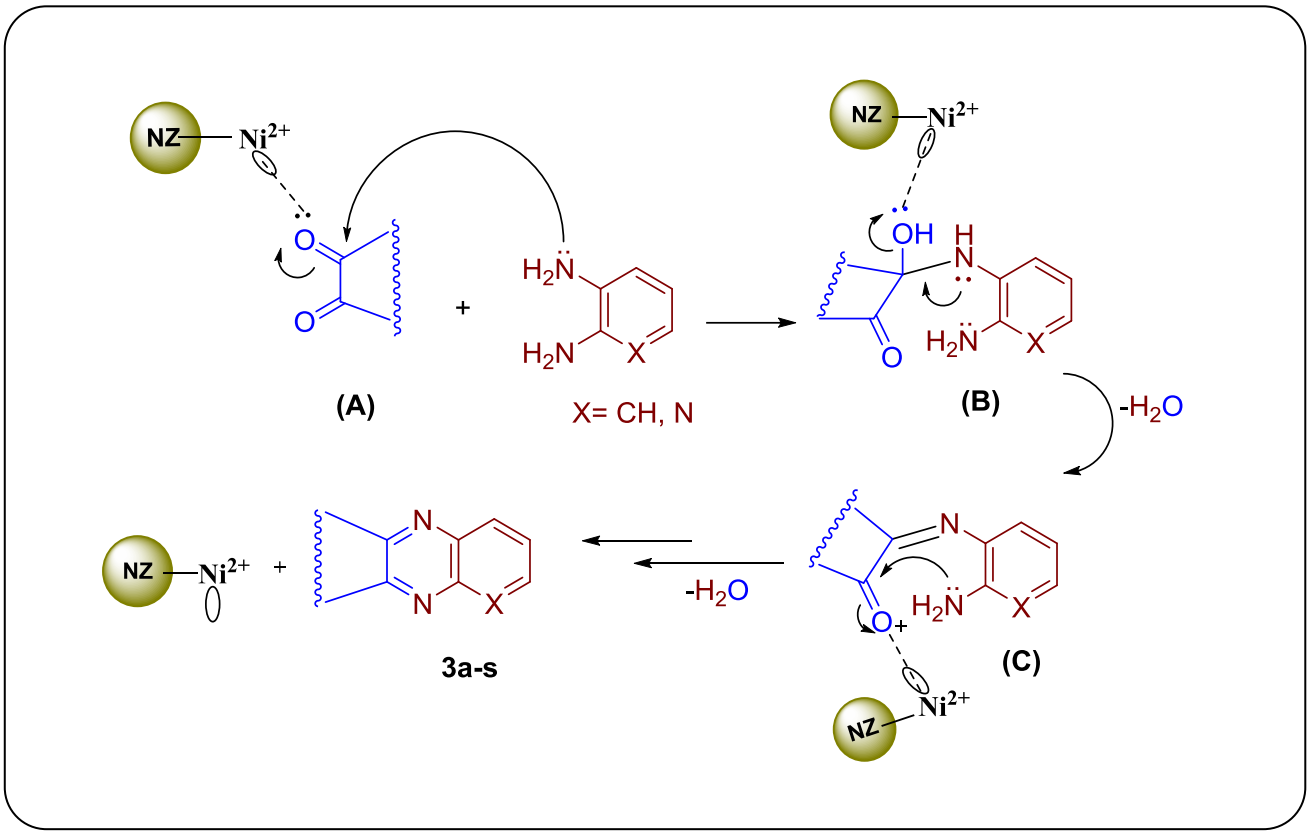


Scheme 2: Synthetic pathway for Compounds (3a–s).

Table 4: The nano-catalyst recovery study in the reaction of model under the optimized conditions (Table 1, entry 3).

Entry	Time (min)	Yield (%)[a]
1	5	95
2	5	92
3	10	88
4	15	85

a) Isolated yield.



Scheme 3. Proposed mechanism for the synthesis of Compounds 3a-s.

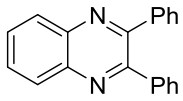
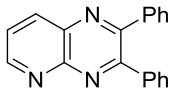
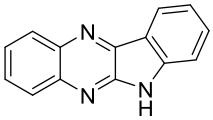
the reaction is completed, in most cases, in shorter time with higher yield in green media and simple work-up (Table 5).

The ^{1}H NMR spectrum of compound **3r** is considered to be simple, in which the resonance of NH proton of indole ring and the six aromatic protons appeared in the regions of 12.75 and 7.58-9.63 ppm. Also, the physical and spectroscopic (FT-IR, ^{1}H-, ^{13}C NMR and Mass spectra) data for a number of selected compounds confirmed the structures of the products.

CONCLUSIONS

Ni@zeolite-Y nanoporous was synthesized, characterized and employed as a mild and high efficient catalyst for the facile conversion of aryl-1,2-diamines, 1,2-diketones, and the isatin to quinoxaline, pyrido[2,3-*b*]pyrazine, and indolo[2,3-*b*]quinoxaline derivatives in EtOH or AcOH at room temperature. The procedure was demonstrated to be simple both in conducting the reaction and in isolating the products. The attractive features of this procedure such as good conversion, reusability

Table 5: Comparison of our results with some previously reported data for the synthesis of compounds 3a, 3d and 3n at room temperature.

Product	Catalyst (Loading, %)	Solvent	Time (min)	Yield (%)	[Ref]
 **3a**	Phenol (20)	EtOH/H_2O	2	98	[59]
	Mont K-10 (10)	H_2O	150	100	[23]
	$ZrCl_4$ (5)	MeOH	5	100	[28]
	Gallium triflate (5)	EtOH	5	99	[24]
	Zn/L-proline (10)	AcOH	5	96	[27]
	Iodine (10)	MeCN	5	95	[20]
	$CuSO_4{\cdot}5H_2O$ (10)	MeOH/ H_2O	5	97	[26]
	Ceric(IV) ammonium nitrate (5)	H_2O	10	98	[21]
	Nano-Ni@zeolite Y (3)	EtOH	5	95	This Work
 **3d**	Phenol (20)	EtOH/H_2O	225	91	[59]
	$ZrCl_4$ (5)	MeOH	60	96	[28]
	TiO_2-P_{25}-SO_4^{2-} (5)	EtOH	60	78	[36]
	$BiCl_3/SiO_2$ (5)	MeOH	30	98	[66]
	Cu-Schiff-base/SBA-15 (10)	H_2O	120[a]	96	[38]
	Nano-Ni@zeolite Y (10)	EtOH	25	90	This Work
 **3n**	-	AcOH	1440[a]	88	[42]
	Sulfamic acid (20)	EtOH	60	83	[43]
	Ce.MCM-41 (30)	-	60	75	[41]
	-	AcOH	60[a]	80	[62]
	Nano-Ni@zeolite Y (10)	AcOH	15	90	This Work

a) It was in under refluxing

and safety of nano-catalyst and easy work-up make it a beneficial manner for the simple synthesis of the target compounds.

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