

RESEARCH PAPER

Ionic liquid-tethered colloidal silica nanoparticles as a reusable and effective catalyst for the synthesis of phenazines

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ARTICLE INFO

Article History:

Received 08 July 2020

Accepted 17 September

Published 15 October 2020

Keywords:

Ionic liquid

Nanocatalyst

Ultrasonic

Phenazines

ABSTRACT

Bis (1(3-trimethoxysilylpropyl)-3-methyl-imidazolium) nickel tetrachloride tethered to colloidal nano-silica (ionic liquid/ colloidal nano-silica) has been used as an effective catalyst for the preparation of benzopyranophenazines through the reaction of hydroxynaphthoquinone, o-phenylenediamine, benzaldehydes, and malononitrile under ultrasonic irradiations in ethanol. The catalyst has been characterized by ¹H NMR, FE-SEM, EDS, DLS and TGA. Experimental simplicity, excellent yields in short reaction times, wide range of products and applying the sonochemical methodology as an efficient method and innocuous means of activation in synthetic chemistry for the synthesis of medicinally privileged heterocyclic molecules are some of the substantial features of this procedure. The present catalytic method is extensible to a wide diversity of substrates for the preparation of a variety-oriented library of phenazines.

How to cite this article

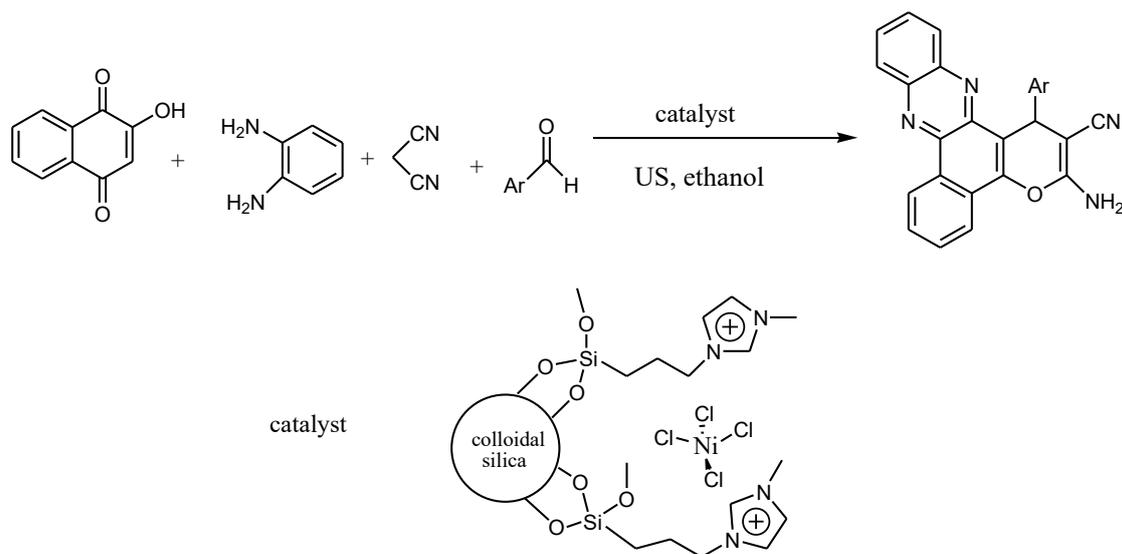
Shahbazi-Alavi H., Safaei-Ghomi J, Dehghan M.D. Ionic liquid-tethered colloidal silica nanoparticles as a reusable and effective catalyst for the synthesis of phenazines. *Nanochem Res*, 2020; 5(2):111-119. DOI: 10.22036/ncr.2020.02.001

INTRODUCTION

The synthesis of heterocycles has always been an essential and growing area of organic chemistry as heterocycle compounds show a various range of biological activities [1-5]. Phenazines exhibit important biological properties such as anti-tumor [6], antibacterial [7], anti-proliferative [8], antifungal [9], and anti-inflammatory [10]. These attributes make phenazines notable targets in organic preparation for future consideration. A number of procedures have been developed for the preparation of phenazines using *p*-TSA [11], glacial acetic acid [12], 1,4-diazabicyclo[2.2.2]octane (DABCO) [13,14], thiourea-based organocatalysts [15], caffeine [16], theophylline [17], L-proline [18], 1-butyl-3-methylimidazolium hydroxide ([Bmim] OH) [19], and Et₃N [20]. Each of these procedures may have its own advantages but also suffer from such apparent drawbacks as prolonged reaction

times, complicated work-up, non-reusable catalyst, low yield, or hazardous reaction conditions. To elude these restrictions, discovery of an efficient, easily accessible catalyst with high catalytic activity for the preparation of phenazines is still favored. In recent years, synthesis and immobilization of nanoparticles in ionic liquids (ILs) have been widely investigated [21,22]. Ionic liquids can be considered as valuable key precursor compounds for catalysts [23, 24]. The nature of cation-anion interactions in ambient temperature ionic liquids is an issue of increasing interest [25,26]. The structures of 1-ethyl-3-methylimidazolium (Emim) and 1-butyl-3-methylimidazolium (Bmim) with transition metal chloride anions including NiCl₄²⁻, CoCl₄²⁻, and PdCl₄²⁻ were investigated [27,28]. Ideally, introducing neat processes and utilizing eco-friendly and green nanocatalysts which can be simply recycled at the end of reactions have received considerable attention in recent years

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Scheme 1. Synthesis of phenazines under ultrasonic irradiations using nanocatalyst

[29-31]. Herein, we reported the preparation of bis (1(3-trimethoxysilylpropyl)-3-methyl-imidazolium)nickel tetrachloride tethered to colloidal silica nanoparticles as a reusable catalyst [28] and investigated its catalytic activity for one-pot multicomponent synthesis of phenazines under ultrasonic irradiations (Scheme 1).

EXPERIMENTAL SECTION

Preparation of 1-(3-trimethoxysilylpropyl)-3-methyl-imidazolium chloride

Ionic liquid was prepared according to the procedure reported in the literature [32].

Preparation of bis (1(3-trimethoxysilylpropyl)-3-methyl-imidazolium) nickel tetrachloride tethered to colloidal nano-silica (ionic liquid/ colloidal nano-silica)

0.098 mL of colloidal silica nanoparticles (LUDOX SM colloidal silica 30 wt. % suspension in H₂O) was diluted in 3 mL of deionized water, and 1.5 mmol of 1-(3-trimethoxysilylpropyl)-3-methyl-imidazolium chloride IL was added slowly with continuous stirring during one hour. Then, 0.18 g of NiCl₂·6H₂O was added and refluxed for 24 h. After 24 h, ionic liquid functionalized colloidal nano-silica was separated by centrifugation and washed with acetone and methanol for four times, then, ionic liquid-tethered colloidal silica nanoparticles were dried by lyophilization/freeze-drying [28].

The purity of the resultant ionic liquid-tethered colloidal silica nanoparticles was confirmed using

¹H NMR spectrum. The Ni loading was measured using XRF to be 3.3 wt%.

General procedure for the preparation of phenazines

A mixture of hydroxynaphthoquinone (1 mmol), *o*-phenylenediamine (1 mmol) aldehydes (1 mmol) and malononitrile (1.5 mmol) and ionic liquid-tethered colloidal silica nanoparticles (8 mg) in EtOH (15 mL) was sonicated at 40 W power in appropriate times. The progress of the reaction was monitored by TLC (EtOAc/*n*-hexane 2:1). After completion of the reaction, the mixture was cooled to room temperature and nanocatalyst was easily separated by centrifuging. The solvent was evaporated and the solid obtained was filtered and then washed with EtOH and water (ratio: 5:5) to afford the pure desired product.

*3-Amino-1-(4-cyano-phenyl)-1H-benzo[*a*]pyrano[2,3-*c*]phenazine-2-carbonitrile (5h)*: Yellow solid, m.p.: 288-290 °C; IR (KBr, ν, cm⁻¹): 3324, 3175, 3045, 2832, 2182, 2138, 1646, 1623, 1482, 1456, 1445, 1394, 1382, 1358, 1339, 1295; ¹H NMR (400 MHz, DMSO-*d*₆) (δ, ppm): 5.43 (s, 1H, CH), 7.25 (s, 2H, NH₂), 7.39 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.43 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.83-8.08 (m, 4H, Ar-H), 8.14-8.17 (m, 1H, Ar-H), 8.18-8.23 (m, 1H, Ar-H), 8.45 (d, 1H, *J* = 7.6 Hz, Ar-H), 9.18 (d, 1H, *J* = 7.2 Hz, Ar-H); ¹³C NMR (100MHz, DMSO-*d*₆) (δ, ppm): 37.4, 57.8, 113.8, 115.2, 118.3, 122.2, 124.4, 125.6, 126.3, 127.7, 128.2, 128.8, 129.0, 129.2, 130.2, 130.3, 130.6, 130.8, 139.9, 140.2, 140.7, 141.3, 145.6, 146.4, 159.5; Anal. Calcd. for C₂₇H₁₅N₅O: C,

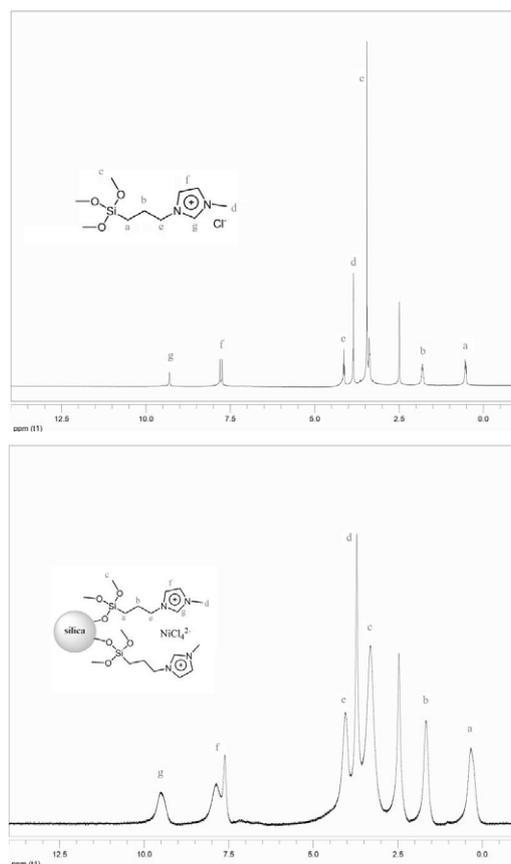


Fig. 1. (a) ^1H NMR spectrum of 1(3-trimethoxysilylpropyl)-3-methyl-imidazolium chloride and (b) bis(1(3-trimethoxysilylpropyl)-3-methyl-imidazolium) nickel tetrachloride tethered to silica nanoparticles (nanocatalyst) in dimethyl sulfoxide (DMSO)

76.22; H, 3.55; N, 16.46; Found: C, 76.17; H, 3.42; N, 16.34.

3-Amino-1-(4-methoxy-phenyl)-1H-benzo[*a*]pyrano[2,3-*c*]phenazine-2-carbonitrile (5m): Yellow solid, m.p.: 268-269 °C; IR (KBr, ν , cm^{-1}): 3316, 3174, 3047, 2828, 2180, 1653, 1622, 1585, 1486, 1465, 1452, 1394, 1354, 1330, ^1H NMR (400 MHz, DMSO-d_6) (δ , ppm): 3.85 (s, 3H, OCH_3), 5.86 (s, 1H, CH), 6.67 (d, 2H, $J = 7.6$ Hz, Ar-H), 6.92 (d, 2H, $J = 7.6$ Hz, Ar-H), 7.35 (s, 2H, NH_2), 7.86-7.94 (m, 4H, Ar-H), 7.99-8.42 (m, 3H), 9.10 (d, 1H, $J = 8.0$ Hz, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6) (δ , ppm): 37.5, 55.3, 58.3, 112.2, 115.3, 115.5, 120.2, 120.5, 121.4, 125.2, 127.2, 129.1, 129.4, 129.7, 130.1, 130.6, 130.8, 130.8, 140.3, 141.3, 141.9, 146.5, 147.3, 159.6, 160.7; Anal. Calcd. for $\text{C}_{27}\text{H}_{18}\text{N}_4\text{O}_2$: C, 75.34; H, 4.21; N, 13.02; Found C, 75.23; H, 4.15; N, 12.95.

RESULTS AND DISCUSSION

Characterization of the nanocatalyst

Figs. 1a and 1b indicate the ^1H NMR spectra for the 1(3-trimethoxysilylpropyl)-3-methyl-imidazolium

chloride and bis(1(3-trimethoxysilylpropyl)-3-methyl-imidazolium) nickel tetrachloride tethered to colloidal silica nanoparticles in dimethyl sulfoxide (DMSO), respectively. The NMR spectra of both materials are consistent with expected results for untethered and silica-tethered ionic liquids.

Fig. 2 displays FE-SEM (Field emission-scanning electron microscopy) image of bis(1(3-trimethoxysilylpropyl)-3-methyl-imidazolium) nickel tetrachloride tethered to colloidal nano-silica (nanocatalyst). The SEM images show particles with diameters in the nanometer range.

In order to study the size distribution of nanocatalysts, DLS (dynamic light scattering) measurements of the nanoparticles were exhibited in Fig. 3. This size distribution is centered at a value of 15.9 nm.

The elemental compositions of the nanocatalyst were studied by EDS (energy dispersive spectroscopy). EDS confirmed the presence of Si,

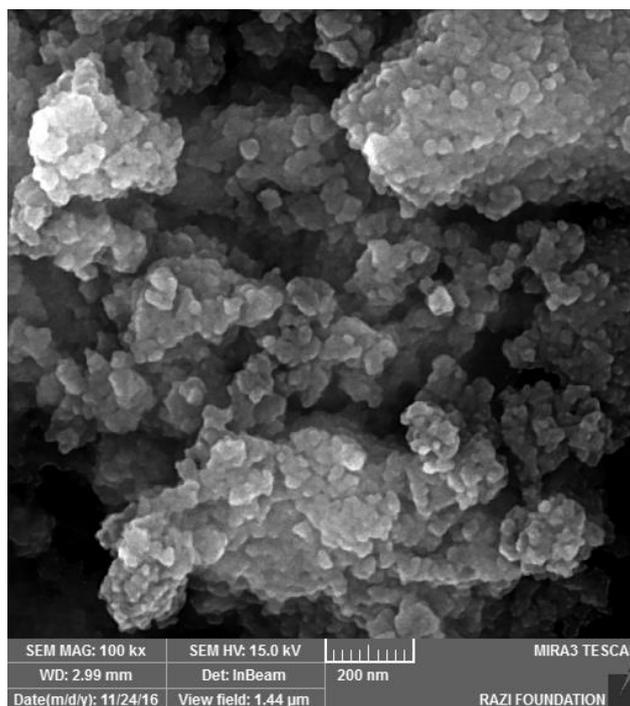


Fig. 2. FE-SEM (field emission-scanning electron microscopy) image of ionic liquid-tethered to silica nanoparticles

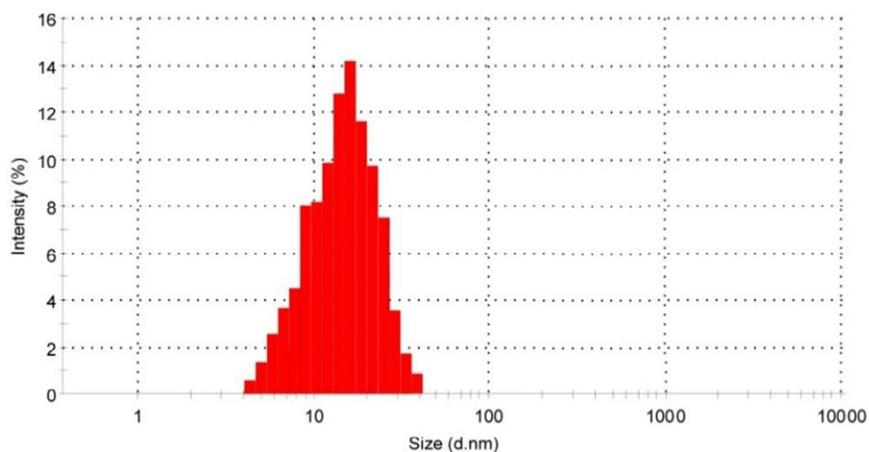


Fig. 3. DLS (dynamic light scattering) of ionic liquid-tethered to silica nanoparticles

O, N, Cl, and Ni in the compound (Fig. 4).

Thermogravimetric analysis (TGA) evaluates the thermal stability of the ionic liquid of untethered to SiO_2 (pure ionic liquid) and silica-tethered ionic liquids (ionic liquid/colloidal nano-silica with molar ratio 2.5 and 5.5). The curve shows a weight loss about 46.62% and 31.73% for ionic liquid/

colloidal nano-silica with molar ratio 5.5 and 2.5, respectively, from 240 to 610 °C, resulting from the decomposition of organic spacer attaching to the nanoparticles. Hence, the nanocatalyst was stable up to 240 °C, confirming that it could be stably utilized in organic reactions at temperatures between the ranges of 90–140 °C (Fig. 5).

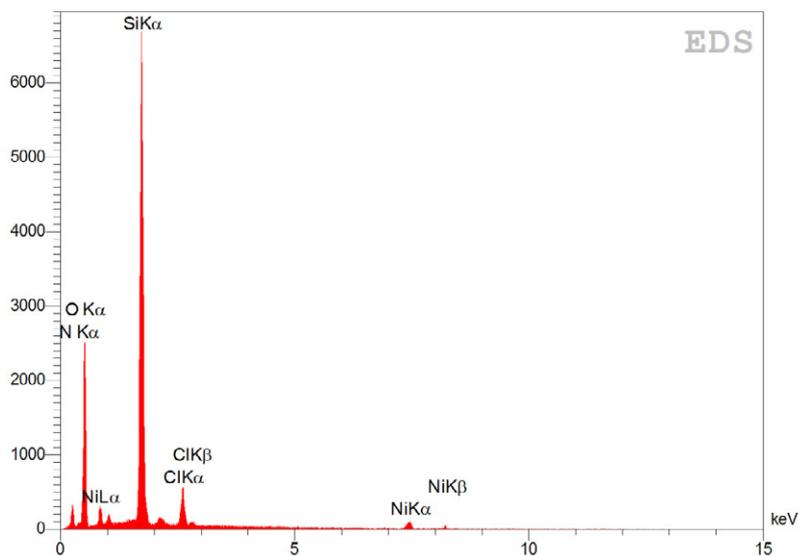


Fig. 4. EDS of ionic liquid-tethered to silica nanoparticles

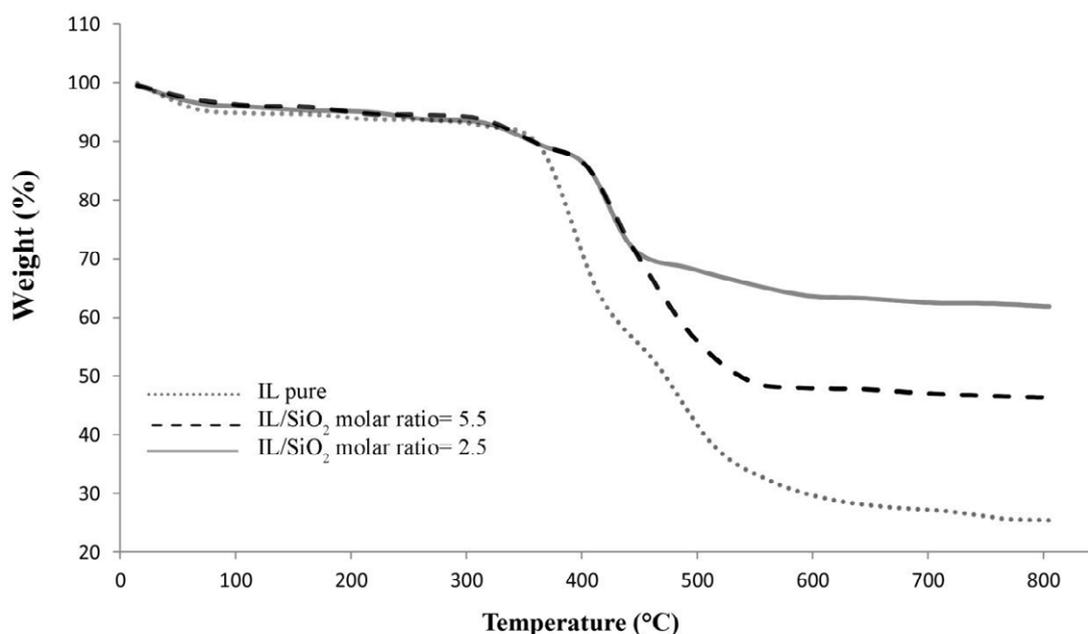


Fig. 5. TGA of ionic liquid-tethered to silica nanoparticles

Investigation of catalytic activity for synthesis of phenazines

Initially, we focused on the systematic evaluation of diverse catalysts for the model reaction of hydroxynaphthoquinone, *o*-phenylenediamine, 4-chlorobenzaldehyde, and malonitrile under different conditions. To obtain the ideal reaction conditions for the synthesis of compound **5b**, we studied some other catalysts and solvents which are

shown in Table 1. Screening of different catalysts containing NiCl₂, imidazole, ZrOCl₂, *P*-TSA, CuCl₂ and nanocatalyst (ionic liquid/colloidal nano-silica) revealed ionic liquid/colloidal nano-silica (with molar ratio 2.5) as the most effective catalyst to perform this reaction under ultrasonic irradiations (40 W) in ethanol. The results illustrated that the sonication certainly affected the reaction system. It could reduce the reaction time and increase the

Table 1. Optimization of reaction conditions using different catalysts under different conditions ^a

Entry	Solvent (conditions)	Catalyst	Time (min)	Yield ^c %
1	EtOH (reflux)	no catalyst	500	trace
2	EtOH (reflux)	NiCl ₂ (5 mol%)	400	40
3	EtOH (reflux)	ZrOCl ₂ (5 mol%)	500	45
4	EtOH (reflux)	imidazole (7 mol%)	400	35
5	EtOH (reflux)	<i>p</i> -TSA (8 mol%)	200	52
6	EtOH (reflux)	CuCl ₂ (5 mol%)	250	47
7	H ₂ O (reflux)	ionic liquid/colloidal nano-silica (15 mg)	150	46
8	DMF (reflux)	ionic liquid/colloidal nano-silica (15 mg)	150	51
9	CH ₃ CN (reflux)	ionic liquid/colloidal nano-silica (15 mg)	150	64
10	EtOH (reflux)	ionic liquid/colloidal nano-silica (15 mg)	150	73
11	H ₂ O (US: 40 W) ^b	ionic liquid/colloidal nano-silica (10 mg)	15	56
12	DMF (US: 40 W)	ionic liquid/colloidal nano-silica (10 mg)	15	67
13	CH ₃ CN (US: 40 W)	ionic liquid/colloidal nano-silica (10 mg)	15	78
14	EtOH (US: 20 W)	ionic liquid/colloidal nano-silica (8 mg)	15	74
15	EtOH (US: 30 W)	ionic liquid/colloidal nano-silica (8 mg)	10	86
16	EtOH (US: 40 W)	ionic liquid/colloidal nano-silica (8 mg)	10	96
17	EtOH (US: 50 W)	ionic liquid/colloidal nano-silica (8 mg)	10	96
18	EtOH (US: 40 W)	ionic liquid/colloidal nano-silica (6 mg)	10	89
19	EtOH (US: 40 W)	ionic liquid/colloidal nano-silica (10 mg)	10	96

^a Reaction conditions: 2-hydroxynaphthalene-1,4-dione (1 mmol), *o*-phenylenediamine (1 mmol), 4-chlorobenzaldehyde (1 mmol), and malononitrile (1.5 mmol) as a model reaction

^b Ultrasonic irradiation

^c Isolated yield

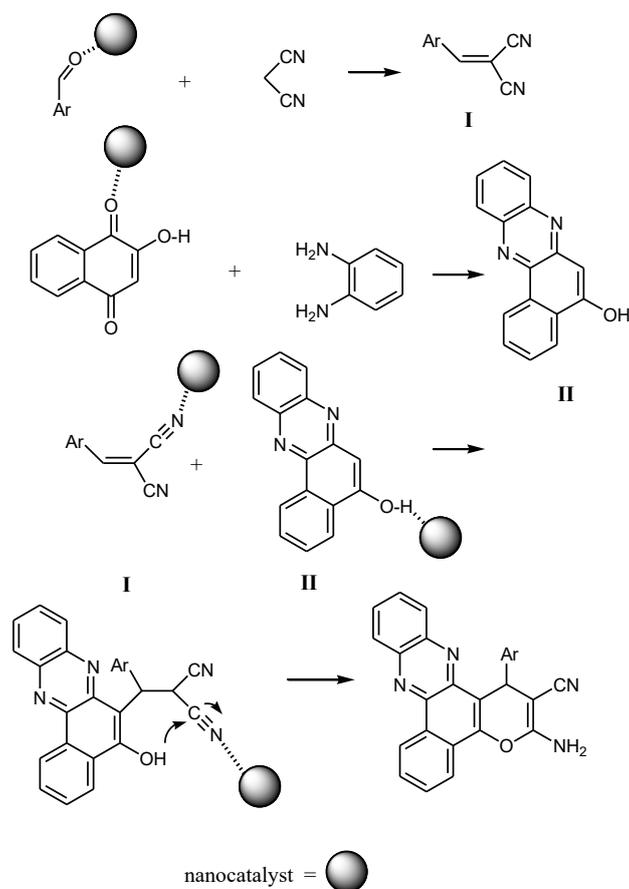
Table 2. Synthesis of benzopyranophenazine derivatives ^a

Entry	R (aldehyde)	Product	Time (min)	Yield ^a (%)	m.p/ ^o C found (reported)
1	H	5a	10	91	297-300 (298-300) [33]
2	4-Cl	5b	10	96	290-292 (288-290) [33]
3	2-Cl	5c	10	93	299-302 (301-303) [33]
4	4-Br	5d	10	97	282-284 (283-285) [33]
5	4-F	5e	10	97	273-276 (274-276) [33]
6	2-NO ₂	5f	10	93	277-281 (278-279) [33]
7	3-NO ₂	5g	10	93	280-282 (281-283) [33]
8	4-CN	5h	10	92	288-290
9	4-NO ₂	5i	15	96	261-263 (261-263) [33]
10	4-Me	5j	15	85	293-295 (293-294) [33]
11	2-OMe	5k	15	81	268-270 (270-272) [33]
12	3-OMe	5l	15	83	239-241 (240-242) [33]
13	4-OMe	5m	15	80	268-269
14	2,4-dichloro	5n	10	96	306-309 (308-310) [33]

^a Isolated yield.

yield of the products. Accordingly, it should be noted that electron-withdrawing groups increased the rate of reaction and gave better yields than those with electron-donating groups. Several functional groups, such as Cl, OMe, CN, and CH₃, are compatible under

the reaction conditions. Interestingly, a variety of aromatic aldehydes, including *ortho*, *meta* and *para*-substituted aryl aldehydes, participated well in this reaction and gave the corresponding products in a good to excellent yield (Table 2).



Scheme 2. Proposed mechanism for the synthesis of benzopyranophenazines

We investigated reusability of the ionic liquid/colloidal nano-silica as a catalyst for the synthesis of product **5b**, and it was found that product yields reduced to a small extent on each reuse (run 1, 96%; run 2, 96%; run 3, 95%; run 4, 95%; run 5, 94%, run 6, 94%). After completion of the reaction, the mixture was cooled to room temperature and nanocatalyst was easily separated by centrifuging. The nanoparticles were then washed four times with dichloromethane and dried at room temperature for 24 h.

To determine the degree of leaching of the metal from the heterogeneous nanocatalyst, the catalyst was removed by filtration and the Ni amount in reaction medium after each reaction cycle was measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The analysis of the reaction mixture by the ICP technique displayed that the leaching of Ni was negligible (the leaching of Ni in five continuous runs was found to be ≤ 0.5 ppm). We believe that

this could be a reason for the extreme stability of the catalyst presented herein.

A proposed mechanism for the synthesis of benzopyranophenazines using nanocatalyst is shown in Scheme 2. (i) The initial condensation of hydroxynaphthoquinone with *o*-phenylenediamine affords intermediate **I**; (ii) Knoevenagel condensation of malononitrile and benzaldehydes to form the intermediate **II**; (iii) The Michael addition of intermediate **I** with intermediate **II** formed intermediate **III**, which in subsequent cyclization and tautomerism affords the corresponding products. In this mechanism, the surface atoms of nanocatalyst activate the C=O and C≡N groups for better reaction with nucleophiles.

CONCLUSIONS

In conclusion, we have reported an efficient method for the synthesis of benzopyranophenazines using ionic liquid/colloidal nano-silica as a superior catalyst under ultrasonic irradiations. The

new catalyst is characterized by ^1H NMR, FE-SEM, EDS, DLS and TGA. The current method provides obvious positive points containing environmental friendliness, reusability of the catalyst, low catalyst loading and use of ultrasonic irradiation as a valuable and powerful technology.

ACKNOWLEDGEMENT

The authors are grateful to University of Kashan for supporting this work by Grant NO: 159196/XXX.

CONFLICT OF INTEREST

The author declares that there is no conflict of interest.

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