IONIC LIQUID-FUNCTIONALIZED TITANOMAGNETITE NANOPARTICLES AS EFFICIENT AND RECYCLABLE CATALYST FOR GREEN SYNTHESIS OF 2,3-DIHYDROQUINAZOLIN-4(1H)-ONES

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Abstract. In the present study, titanomagnetite nano-particles ($Fe_{3-x}Ti_xO_4$ NPs) were synthesized *via* coprecipitation approach and then functionalized using 3-trimethoxysilylpropyl chloride silan coupling agent followed by tetrabutylammonium asparaginate through a facial and newly one-pot procedure to afford an ionic liquid (IL)-modified $Fe_{3-x}Ti_xO_4$ NPs. The synthesized NPs were examined as potent and recyclable nanocatalysts for one-pot three-component synthesis of 2,3-dihydro-quinazolin-4(1H)-ones under solvent-free conditions. Easy magnetic separation and efficient recyclability of the catalyst, excellent yields of the reactions, low reaction times as well as solvent-free conditions are the most important advantages of the present procedure that qualified the fabricated $Fe_{3-x}Ti_xO_4$ NPs as a nanocatalyst for industrial applications.

Keywords: ionic liquid, titanomagnetite nanoparticles, nanocatalyst, green chemistry, organic synthesis.

1. Introduction

Among the heterogeneous catalysts reported in the literature for the synthesis of organic compounds, inorganic nanoparticles (NPs) (*e.g.*, magnetic NPs) are of considerable interest as efficient catalysts and supports. This intense interest is originated from their extraordinary properties including a nano-scaled size, high surface-to-volume ratio, and coordinated parts which provide a large number of active sites per unit area in comparison with their corresponding microparticles [1, 2].

It is an unquestionable fact that the use of homogeneous catalysts are subjected to tedious separation by filtration or centrifugation that is required to avoid the contamination of the final products with residual metal

especially in the case of pharmaceuticals [3]. In addition, from economic and environmental points of view, the design and development of recyclable and eco-friendly heterogeneous catalysts is necessary for industrial processes. In this respect, magnetic (MNPs) have found applications as catalysts or supports for various reactions [4-8]. In recent years, numerous metal oxide NPs with high performance of magnetic properties have been developed and widely used as magnetic data storage, bio/chemical sensors, environmental sciences, sorbents, biomedical fields, as well as catalysts [9-12]. In this context, titanomagnetite ($Fe_{3-x}Ti_xO_4$) NPs is of particular interest, because the presence of Ti^{4+} cations in its structure leads to significant increasing the relative number of surface hydroxyl groups [13]. It is well established that, incorporation of some transient metals (*e.g.*, Mn, Cr, Co, V, and Ti) into Fe_3O_4 NPs significantly improve their physicochemical features. These nanomaterials have received a great deal of scientists attentions for different applications such as environmental engineering, mineralogy and material sciences [13-18].

Nevertheless, the main issue regarding the application of these NPs is their quick aggregation into large bunches that lead to lose their unique properties. This thematic issue can be solved through the surface modification using organic or inorganic components such as SiO_2 or silan coupling agents to form core-shell structures [19-21].

On the other hand, the surface modification of these NPs using ionic liquids (ILs) is another strategy for improving the catalytic function of these nanomaterials in organic reactions and industrial processes. The promising advantages of this strategy are environmental benignity, high thermal stability, high catalytic efficiency, reusa-bility, negligible vapor pressure, low viscosity, easy handling and separation from the products due to their heterogeneous behavior [22-25].

Quinazolinone has attracted great deal of academic and industrial interest as an exciting motif mainly due to its pharmacological and therapeutic importance as an

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effective anticonvulsant [26], anti-inflammatory [27, 28], analgesic and cyclooxygenase-2 (COX-2) inhibitor [29-33], anti-cancer [34, 35], anti-hypertensive [36], anti-malarial [37], antimicrobial [38] and diuretic activities [39]. In addition, quinazolinone nucleus exists as a building block in many naturally occurring alkaloids [40]. 2,3-Disubstituted quinazolin-4(3H)-ones have been reported to exhibit remarkable anticonvulsant, analgesic and anti-inflammatory activities. Also, 1,2-dihydroquinazolinones were reported to possess greater potent activity compared to fully aromatic quinazolinones [41].

Numerous strategies have been reported for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones in the literature using various catalytic systems and reaction conditions [42-52]. In this investigation, IL-modified $Fe_{3-x}Ti_xO_4$ NPs were applied as a recyclable and heterogeneous nanocatalyst for the one-pot three-component synthesis of 2,3-dihydroquinazolin-4(1H)-onesunder solvent-free conditions. The effect of some parameters including solvent, time, and temperature on the yield of reactions was also examined.

# 2. Experimental

2.1. General

All solvents used were strictly dried according to standard operations and stored over 4Å molecular sieves. Other chemicals were purchased from Merck (Darmstadt, Germany) and used as received without further purification. Melting points were determined in open capillaries using a BUCHI 510 apparatus (Flawil, Switzerland). Fourier transform infrared (FTIR) spectra were recorded using KBr pellets on a Shimadzu 435-U-04 FT-IR spectrometer (Kyoto, Japan). ^{1}H and ^{13}C NMR spectra were obtained on 400 and 100 MHz Bruker instrument (Bruker, Ettlingen, Germany), respectively, in DSMO-d_6 as a solvent and tetramethylsilane (TMS) as an internal standard. Mass spectra (MS) were recorded by a FINNIGAN-MAT 8430 spectrometer (Bremen, Germany) operating at an ionization potential of 70 eV.

2.2. Catalyst Synthesis

2.2.1. Synthesis of tetrabutylammonium asparaginate (TBAAsp) ionic liquid

Tetrabutylammonium asparaginate ionic liquid was synthesized according to previously reported modified procedure [53] (Scheme 1) as follows: a solution of *L*-asparagine amino acid (2.64 g, 20 mmol) in distilled water (20 ml) was ultrasonicated for 20–30 min at room temperature to give an aqueous suspension. Then, an

aqueous solution of tetrabutylammonium hydroxide (TBAOH; 40 % w/v; 5.2 ml; 20 mmol) was added under vigorous stirring and the resulted mixture was refluxed for 24 h. Afterward, the mixture was cooled to room temperature, the water was removed using a rotary evaporator under reduced pressure and the mixture containing unreacted asparagine amino acid and desired ionic liquid was diluted with chloroform (10 ml). Finally, the mixture was filtered to separate the remaining amino acid, and the filtrate was dried in air to yield the yellow viscose ionic liquid. The spectral data (^{1}H NMR, ^{13}C NMR and MS) of the synthesized ionic liquid are given below.
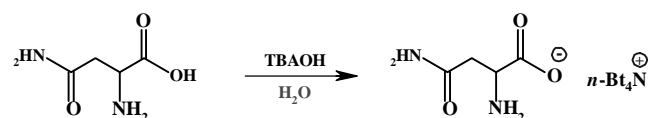
**Scheme 1.** Synthesis of tetrabutylammonium asparaginate (TBAAsp) ionic liquid

Spectral data of the synthesized tetrabutylammonium asparaginate (TBAAsp) ionic liquid. Yellow viscose liquid. FTIR (KBr) ν: 3383, 3295, 2967, 2941, 2875, 1667, 1578, 1490, 1468, 1366 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.95 (t, 12H, 4CH$_3$), 1.31-1.33 (m, 8H, 4CH$_2$), 1.58 (m, 8H, 4CH$_2$), 1.88-1.95 (dd, 1H , H$_2$NC(O)-CH), 2.42-2.43 (dd, 1H , H$_2$NC(O)-CH), 3.17-3.22 (m, 8H, 4CH$_2$), 3.59 (dd, 1H, H$_2$N-CH), 5.1, 6.32 (4H, 2NH$_2$) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ:13.9 (CH$_3$), 19.7 (-CH$_2$), 23.6 (-CH$_2$), 44.3 (CH$_2$), 54.2 (HC-NH$_2$), 57.9(-CH$_2$), 174.9 C(O)-NH$_2$), 175.4 (COO$^-$) ppm. MS (70 eV), *m/z* =373.4.

2.2.2. Synthesis of $Fe_{3-x}Ti_xO_4$ MNPs

Titanomagnetite nanoparticles ($Fe_{3-x}Ti_xO_4$ NPs) were synthesized following the approach reported in the literature [16, 55]. A solution of FeSO$_4$·7H$_2$O (3.81 g, 13.6 mmol) in deionised water (18 ml) was prepared and its pH value was adjusted to < 1 by adding HCl solution (1M; 7 ml). TiCl$_4$ (1.6 ml) and hydrazine monohydrate (2 ml) were added dropwise to this solution. The resulted mixture was refluxed at 363 K for 30 min under inert atmosphere. Then, an aqueous solution of NaOH (4.0 g) and NaNO$_3$ (2.0 g) in 18 ml of deionised water was added to the mixture under vigorous stirring and refluxed for 1 h. Finally, the resulting mixture was cooled to room temperature using ice/water bath to precipitate the titanomagnetite nanoparticles which were magnetically separated, washed with distilled water and dried under reduced pressure at room temperature.

2.2.3. Synthesis of IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$MNPs

The surface of the synthesized Fe$_{3-x}$Ti$_x$O$_4$ NPs was functionalized using 3-trimethoxysilylpropyl chloride (TMSP-Cl) followed by the synthesized tetrabutyl-ammonium asparaginate ionic liquid *via* a facial one-pot process [54]. For this purpose, Fe$_{3-x}$Ti$_x$O$_4$ NPs (0.61 g) were dispersed in pyridine (20 ml) under ultrasonication for about 30 min. Then, a small amount of sodium metal, 3-chloropropyltrimethoxysilane (1 ml, 5.5 mmol), and a solution of tetrabutylammonium asparaginate (2.04 g, 5.5 mmol in 5 ml of chloroform) were added into the reaction mixture under argon atmosphere. The resulted mixture was ultrasonicated for 20 min. Eventually, the reaction mixture was stirred under reflux condition at 383 K for 24 h. At the end of this time, the modified NPs were separated using a magnetic bar, washed with ethanol, and dried in reduced pressure at room temperature to afford a light brown powder (Scheme 2).
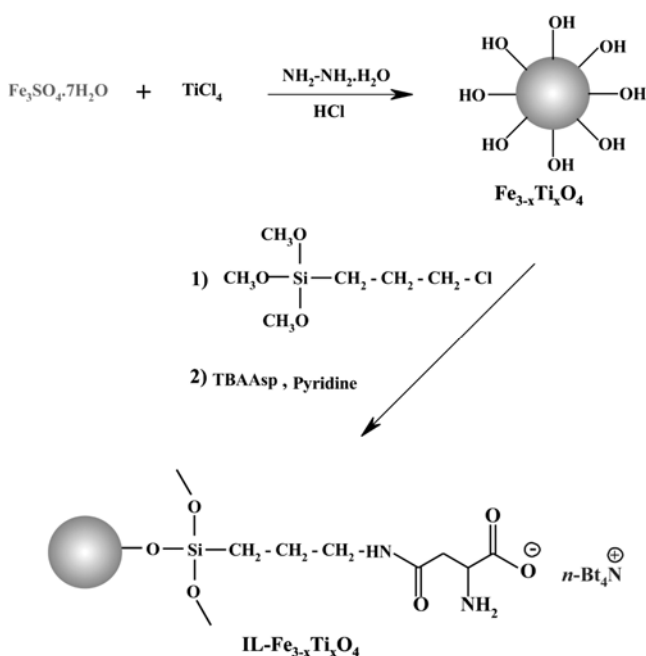
Scheme 2. Synthesis of IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ MNPs

2.2.4. Typical procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives

A 10-ml round-bottom flask was charged with 4-chloroaniline (or ethylamine) (1 mmol), 1*H*-benzo[d][1,3]oxazine-2,4-dione; 2*H*-3,1-benzoxazine-2,4(1*H*)-dione (isatoic anhydride) (0.163 g, 1 mmol), aldehyde (1 mmol), and IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ catalyst (0.01 g). The mixture was stirred at 353 K under solvent-free condition for an appropriate time (*vide* Table 2). After completion of the reaction as monitored by a tine layer chromatography (TLC), the mixture was cooled to room temperature, diluted with ethanol (10 ml), and stirred for other 10 min. Then, the catalyst was separated magnetically simply using an external magnetic bar. The crude product was recrystallized from ethanol to obtain the pure product. All the synthesized products **4a-j** were known compounds which were characterized by their melting points and spectral (FTIR, ^{1}H and ^{13}C NMR) analyses and compared with corresponding reported data as summarized in Table 2.

2.2.5. Selected analytical data

3-(4-Chlorophenyl)-2-phenyl-2,3-dihydroquinazolin-4(1H)-one **(4a)**. Mp. 492–495 K, FTIR (KBr) ν: 3298, 3064, 2834, 1633,1612, 1511, 1491, 1394, 754cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 6.39 (s,1H, CH), 6.83-7.78 (m, 14H, NH and Ar-H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): 72.4, 114.7, 114.9, 117.5, 126.6, 127.9, 128.0, 128.4, 128.5, 128.6, 130.1, 133.9, 139.4, 140.2, 146.6, 162.3 ppm.

3-(4-Chlorophenyl)-2-(4-methylphenyl)-2,3-dihydroquinazolin-4(1H)-one **(4b).** Mp. 529–532 K, FTIR(KBr)ν: 3302, 3069, 2952, 1652, 1634, 1608, 1507, 1491, 1387, 752, 694, 576cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 2.22 (s, 3H, CH$_3$), 6.26 (s,1H, CH), 6.74–7.72 (m, 13H, NH and Ar-H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 20.5, 72.2, 114.7, 115.0, 117.4, 126.5, 127.9, 128.3, 128.4 128.9, 130.0, 133.8, 137.3, 137.7, 139.5, 146.6, 162.3 ppm.

3-(4-Chlorophenyl)-2-(4-fluorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one **(4c).** Mp. 514–517 K, FTIR (KBr) ν: 3302, 3061, 3181, 2929, 1639, 1610, 1507, 1491, 1387, 757 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 6.35 (s, 1H, CH), 6.76-7.72 (m, 13H, NH and Ar-H) ppm.^{13}C NMR (100 MHz, DMSO-d_6): 71.8, 114.8, 115.1, 115.3, 117.6, 127.9, 128.2, 128.5, 128.9, 130.2, 133.9, 136.4, 139.2, 146.6, 162.3, 163.1 ppm.

2-(2-Chlorophenyl)-3-ethyl-2,3-dihydroquinazolin-4(1H)-one **(4h).** Mp. 413–415 K, FTIR (KBr)ν: 3267, 3032, 1620, 1580, 1523, 1470, 1324, 750 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.37-1.40 (d, 3H, CH$_3$), 2.78-2.92 (m, 1H, CH$_2$), 3.71-4.20 (m, 1H, CH$_2$), 5.00-5.04 (s, 1H, NH), 6.11 (s, 1H, CH), 6.45-8.05 (m, 8H, Ar-H) ppm.

3-Ethyl-2-phenyl-2,3-dihydroquinazolin-4(1H)-one **(4i).** Mp. 407–409 K, FTIR (KBr) ν: 3265, 3032, 2969, 1619, 1577, 1469, 1323, 750 cm^{-1}.^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.08-1.23 (d, 3H, CH$_3$), 2.84-2.98 (m, 1H, CH$_2$), 3.83-3.97 (m, 1H, CH$_2$), 4.63 (s, 1H, NH), 5.76 (s, 1H, CH), 6.50-7.95 (m, 9H, Ar-H) ppm.

3-Ethyl-2-(naphthalen-1-yl)-2,3-dihydroquinazolin-4(1H)-one **(4j).** Mp. 407–409 K, FTIR (KBr) ν: 3312,

3058, 2980, 1629, 1612, 1577, 1488, 11414, 778 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.21-1.31 (d, 3H, CH$_3$), 2.73-2.84 (m, 1H, CH$_2$), 3.98-4.06 (m, 1H, CH$_2$), 4.55 (s, 1H, CH), 6.42-8.41 (m, 12H, NH and Ar-H) ppm.

3. Results and Discussion

3.1. Characterization
of the IL-Functionalized Fe$_{3-x}$Ti$_x$O$_4$ NPs

The FTIR spectroscopy was employed to investigate the successful fabrication of the IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ nanocatalyst. The FTIR spectra of the TBAAsp (a) Fe$_{3-x}$Ti$_x$O$_4$ NPs (b), and IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ NPs (c) are shown in Fig. 1. The FTIR spectrum of the TBAAsp (Fig. 1a) shows the characteristic stretching vibrations of –NH$_2$ at 3383–3295 cm^{-1} region, aliphatic C–H stretching vibrations at 2962 and 2875 cm^{-1}, and the carbonyl stretching vibrations of amide and carboxylate at 1667 and 1578 cm^{-1}, respectively. The bands at 1468 and 1366 cm^{-1} are related to the –CH bending vibrations. The FTIR spectrum of Fe$_{3-x}$Ti$_x$O$_4$ NPs exhibited a broad vibrational band at 3418 cm^{-1} that related to the surface hydroxyl stretching vibration. The stretching vibration of Fe–O and Ti–O appeared at 587 and 735 cm^{-1}, respectively.
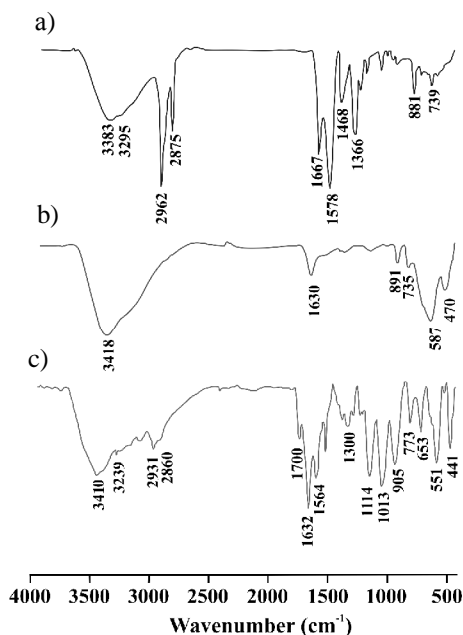

Fig. 1. FTIR spectra of TBAAsp (a), Fe$_{3-x}$Ti$_x$O$_4$ NPs (b), and IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ nanocatalyst (c)

The successful modification of Fe$_{3-x}$Ti$_x$O$_4$ NPs using silan coupling agent followed by TBAAsp is confirmed through the appearance of new characteristic band in the FTIR spectrum of the IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ NPs as follows: the stretching vibrations of C–H at 2931 and 2860 cm^{-1}, and the carbonyl stretching vibrations of amide and carboxylate at 1632 and 1564 cm^{-1}, respectively. In addition, the stretching vibrations of Fe–O and Ti–O at 587 and 735 cm^{-1}, respectively are shifted to relatively lower frequencies (551 and 653 cm^{-1}, respectively) after modification process. This phenomenon is originated from the reduced π-interaction between metal atoms and the non-bonding electrons on the oxygen atoms that lead to formation of Fe–O–Si and Ti–O–Si groups. These FTIR spectra clearly confirm the successful synthesis of IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ NPs.

Further structural information obtained from other analytical techniques including energy dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM), vibrating sample magnetometer (VSM) measurement, as well as thermal gravimetric (TGA) and derivative thermal gravimetric (DTA) analyses have been previously reported [54].

3.2. Catalytic Activity
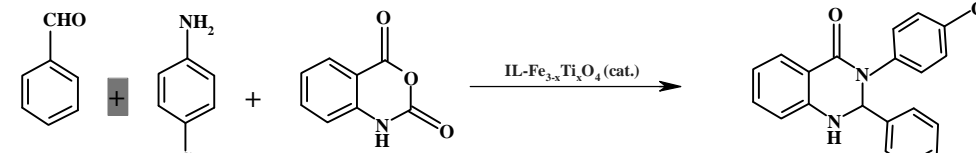## of the IL-Functionalized Fe$_{3-x}$Ti$_x$O$_4$

Primarily, in order to optimize the experimental conditions in terms of the reaction time and yield, the one-pot three-component reaction between benzaldehyde, 4-chloroaniline, and isatoic anhydride was chosen as a model reaction. The results obtained are summarized in Table 1. The experimental data revealed that the optimal condition is achieved when the reaction was performed using 10 mg of the nanomagnetic catalyst at 353 K under solvent-free condition (entry 11). No improvements in the reaction time and yield were observed using higher (entries 3 and 10) or lower (entry 12) amounts of the catalyst under the same conditions. The indispensability of the IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ NPs as the catalyst in the reaction was approved by performing the reaction in the absence of the catalyst which resulted in no detectable amount of the respective product (entry 13).

In regard to the high catalytic performance of IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ NPs presented in the model reaction, the scope and generality of this reaction was investigated using variously substituted aromatic aldehydes (**1a-j**) with two different amines (4-ClC$_6$H$_4$NH$_2$ and C$_2$H$_5$NH$_2$) under optimized conditions (Scheme 3, Table 2). On the basis of the experimental results illustrated in Table 2, all the reactions proceeded smoothly irrespective of the nature of the substituents to furnish the relevant products **4a-j** in excellent yields (92–98 %), and reasonably low reaction times regardless of the substituent nature. In addition, it is clear that the developed IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ NPs can catalyze the reaction with aliphatic amines as effectively as with anilines. Among the products, the known compounds are

characterized on the bases of their physical and spectral (FTIR, ^1H and ^{13}C NMR) data and compared with the corresponding reported data (Table 2).

Optimization of the reaction parameters for synthesis of 2,3-dihydroquinazolin-4(1*H*)-one derivatives using IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ MNPs as the catalyst

Entry	Solvent	Catalyst, mg	Temperature, K	Time, min	Isolated yield, %
1	Solvent-free	30	298	180	30
2	Solvent-free	30	333	120	65
3	Solvent-free	30	353	60	83
4	Solvent-free	30	373	70	80
5	Solvent-free	30	383	70	73
6	EtOH	30	353	180	20
7	H$_2$O	30	353	180	15
8	CH$_3$CN	30	353	120	27
9	EtOH/H$_2$O (1:1)	30	Reflux	150	51
10	Solvent-free	20	353	60	86
11	Solvent-free	10	353	52	92
12	Solvent-free	5	353	70	80
13	Solvent-free	No catalyst	353	120	trace

Reaction conditions: benzaldehyde (0.106 g, 1 mmol), 4-chloroaniline (0.128 g, 1 mmol), isatoic anhydride (0.163 g, 1 mmol), solvent (5 ml).
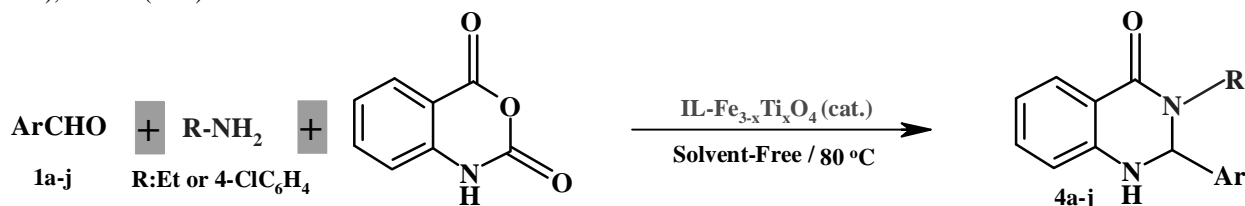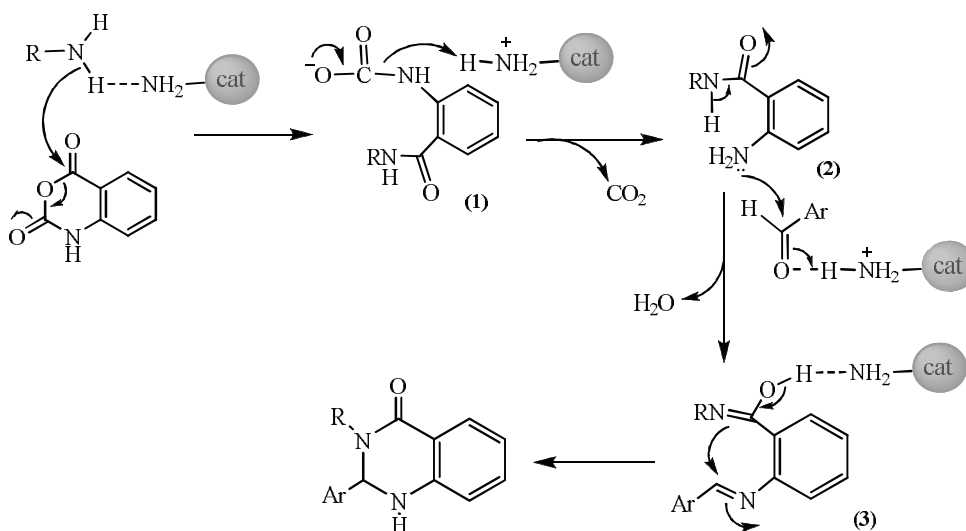

Scheme 3. IL-Fe$_{3-x}$Ti$_x$O$_4$ MNPs-catalyzed synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones **4a-j**

Synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones catalyzed by IL-Fe$_{3-x}$Ti$_x$O$_4$MNPs under solvent free condition

Entry	Ar	R	Product	Time, min	Isolated pure yield, %	Mp, K	
						Found	Reported [44, 56]
1	C$_6$H$_5$	4-ClC$_6$H$_4$	**4a**	52	92	492–495	491–493
2	4-MeC$_6$H$_4$	4-ClC$_6$H$_4$	**4b**	85	96	529–532	531–533
3	4-FC$_6$H$_4$	4-ClC$_6$H$_4$	**4c**	48	94	517–519	516–518
4	3-NO$_2$C$_6$H$_4$	4-ClC$_6$H$_4$	**4d**	85	97	520–522	523–524
5	4-NO$_2$C$_6$H$_4$	4-ClC$_6$H$_4$	**4e**	90	94	526–528	529–531
6	4-BrC$_6$H$_4$	4-ClC$_6$H$_4$	**4f**	85	98	514–517	525–527
7	4-HOC$_6$H$_4$	4-ClC$_6$H$_4$	**4g**	85	92	483–485	539–541
8	C$_6$H$_5$	C$_2$H$_5$	**4h**	48	98	407–410	407–409
9	2-ClC$_6$H$_4$	C$_2$H$_5$	**4i**	35	98	406–409	419–422
10	1-naphthyl	C$_2$H$_5$	**4j**	46	96	460–463	461–463

Reaction conditions: aldehyde (1 mmol), 4-chloroaniline or ethylamine (1 mmol), isatoic anhydride (1 mmol), solvent-free, catalyst (10 mg), $T = 353$ K

Scheme 4. A possible pathway for the synthesis
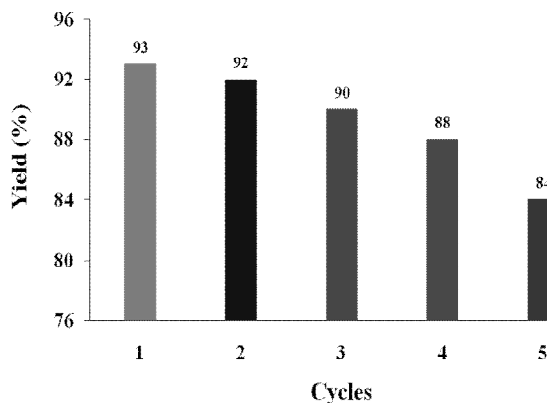of 2,3-dihydroquinazolin-4(1*H*)-ones catalysed by IL-Fe$_{3-x}$Ti$_x$O$_4$ MNPs

Fig. 2. Catalytic reusability of IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ MNPs in the synthesis
of 3-(4-chlorophenyl)-2-(4-bromophenyl)-2,3-dihydroquinazolin-4(1*H*)-one

3.3. Catalytic Reaction Mechanism

A tentatively proposed mechanism to describe one-pot three-component reaction between aromatic aldehydes, 4-chloroaniline (or ethylamine) and isatoic anhydride in the presence of IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ NPs as a basic catalyst is depicted in Scheme 4.

First, the catalyst-accelerated deprotonation and nucleophilic attack of the amine to isatoic anhydride to produce the corresponding carbamate intermediate (**1**). In the next step, decarboxylation of the intermediate (**1**) occurs to yield the 2-aminobenzamide intermediate (**2**). Eventually, the catalyst-activated condensation of the intermediate (**2**) with the aldehyde and the intramolecular cyclization of the resulted 2-(arylideneamino)benzimidic acid intermediate (**3**) take place consecutively to afford the respective products (2,3-dihydroquinazolin-4(1*H*)-ones).

3.4. Regeneration and Reusability of a Catalyst

The regeneration and reuse of a catalyst is important from materials science, ecological, and economic points of view. Therefore, the recycling potential of IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ NPs was examined using the model reaction between 4-bromophenyl aldehyde, isatoic anhydride and 4-chloroaniline under the optimal conditions. After completion of the reaction, the catalyst was magnetically separated from the reaction mixture using an external magnet. The isolated NPs were washed with ethanol three times, dried in vacuum at room temperature. The efficiencies of developed catalyst undergoing five cycles are summarized in Fig. 2. As seen, the IL-functionalized Fe$_{3-x}$Ti$_x$O$_4$ NPs showed a relatively good reusability for at least five fresh times.

4. Conclusions

The developed IL-functionalized $Fe_{3-x}Ti_xO_4$ NPs were applied as an efficient catalyst for one-pot three-component condensation between aromatic aldehydes, isatoic anhydride and 4-chloroaniline (or ethylamine) for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones. The most important advantages of the present protocol include solvent-free and mild reaction condition, excellent yields, as well as relatively low reaction times and easy set-up. The experiments revealed that the developed IL-functionalized $Fe_{3-x}Ti_xO_4$ NPs has a high potential as a catalyst in organic synthesis due to easy synthesis, the uniform distribution of catalytic active species within the supported IL, high stability and selectivity, easy separation from reaction mixtures using an external magnet, and efficient recyclability and reusability.

Acknowledgments

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ЙОННІ РІДКОФУНКЦІОНАЛІЗОВАНІ ТИТАНОМАГНЕТИТНІ НАНОЧАСТИНКИ ЯК ЕФЕКТИВНИЙ І ВІДНОВЛЮВАЛЬНИЙ КАТАЛІЗАТОР ЗЕЛЕНОГО СИНТЕЗУ 2,3-ДИГІДРОХІНАЗОЛІН-4(1Н)-ОНУ

Анотація. Методом ко-осадження синтезовано наночастинки титаномагнетиту ($Fe_{3-x}Ti_xO_4$ NPs) та проведено їх функціоналізацію з використанням 3-триметоксиліл-пропілхлоридного силанового агента і аспарагінату тетрабутиламонію за допомогою нового однореакторного синтезу з метою одержання $Fe_{3-x}Ti_xO_4$ NPs, модифікованих йонною рідиною. Встановлено, що синтезовані NPs є ефективним і відновлювальним нанокаталізатором однореакторного трикомпонентного синтезу 2,3-дигідрохіназолін-4(1Н)-ону без використання розчинників. Показано, що легкість магнітної сепарації та ефективна відновлюваність каталізатора, високі виходи реакцій, малий час реакції, та відсутність розчинників є найважливішими перевагами нового методу. Синтезовані $Fe_{3-x}Ti_xO_4$ NPs можна використовувати як нанокаталізатор у промисловості.

Ключові слова: йонна рідина, наночастинки титаномагнетиту, нанокаталізатор, зелена хімія, органічний синтез.