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Amino acid-based ionic liquid immobilized on α-Fe_2O_3-MCM-41: An efficient magnetic nanocatalyst and recyclable reaction media for the synthesis of quinazolin-4(3H)-one derivatives

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ABSTRACT

For the first time, we report the synthesis and the application of magnetic nanocatalyst (α-Fe_2O_3)-MCM-41-L-prolinium nitrate which was characterized by XRD, TEM, IR, X-ray energy diffraction (XED) spectra and nitrogen physisorption measurements. L-prolinium nitrate (fully green amino acid-based ionic liquid) inside the mesochannels of (α-Fe_2O_3)-MCM-41 lead to prepare a new solid catalyst which was used as an efficient heterogeneous catalyst for the one-pot oxidative cyclization straight synthesis of quinazolin-4(3H)-one derivatives from isatoic anhydride, aldehyde or alkyl halide and primary amines under mild reaction conditions without using any oxidant with good to excellent yields. Moreover, it was proven that in these reactions, the use of such a hybrid material as a catalyst plays the role of rendering the reactions while neither the (α-Fe_2O_3)-MCM-41 nor the L-prolinium nitrate were not able to promote this reaction in the desired pathway toward the above mentioned product. The characteristic features of this catalyst are attributed to both acidic and oxidative behavior of the catalyst.

1. Introduction

Recently, mesoporous materials have attracted significant attention in the field of adsorption, catalysis, and separation as they exhibit extraordinary properties such as a high surface area up to 1500 $m^2 g^{-1}$, a large pore volume, high efficiency, sustainability, and recyclability. MCM-41 (Mobil Composition of Matter No. 41) as a mesoporous material consists of a hexagonal array of unidirectional pore structures. This material is neutral in charge and exhibits only weak hydrogen-bonding type sites which limit its application in catalysis [1–5].

Very recently, the integration of functionalized mesoporous silica with magnetic nanoparticles to form porous magnetic nanostructures has undoubtedly gained much interest for practical applications. This type of magnetic nanostructures has the advantage of both mesoporous silica and magnetic nanoparticles by which magnetic separation with using appropriate magnetic field provides a convenient and low cost method for separating and recycling these magnetic catalysts in a multiphase suspension without using extra organic solvents, additional filtration steps and/or tedious work-up [6].

Development of organocatalytic processes in which the reactions are catalyzed by small organic molecules has become an area of great importance in current organic synthesis particularly from the green chemistry points of view [7]. Ionic liquids (ILs) have attracted increasing attention because of their broad range of applications as reaction medium and promoter in organic chemistry [8]. L-prolinium nitrate is an amino acid-based ionic liquid which exhibits the same characteristics as conventional ionic liquids and, most importantly, it is derived from non-toxic natural products. This ionic liquid with both acidic and chiral characteristics plays an important role in many catalyzed chemical reactions [9] while being used instead of conventional volatile organic solvents to make the system greener and more sustainable. Recently, ionic liquids have been used in the preparation of IL modified materials and several categories of inorganic and hybrid materials [10,11]. Moreover, the synthesis of fine chemicals through the use of supported ILs has been an active area of research in organic chemistry. Immobilized ionic liquids are mainly prepared by two methods: they may be bound covalently to the supporting material surface [12] or they are made by non-covalent binding based on various intermolecular forces between the ILs and the supports, including Van der Waals forces, π-stacking interactions, hydrogen bonding and Coulombic forces [13].

Quinazolin-4(3H)-one derivatives are an important class of heterocycles with a wide range of pharmacological and biological activities [14] and their syntheses have widely been explored. In

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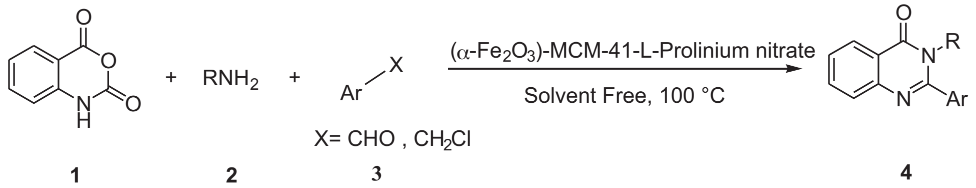


Scheme 1. (α-Fe_2O_3)-MCM-41-L-prolinium nitrate as a magnetic nanocatalyst for the synthesis of quinazolin-4(3H)-one derivatives.

many of the reported methods stoichiometric or excess amounts of oxidants such as DDQ [15], $CuCl_2$ [16], MnO_2 [17], $KMnO_4$ [18], I_2/KI [19], Yb(OTf)$_3$ [20], and solvent as oxidant [21] have been used.

Filling of the mesochannels in mesoporous materials with ILs was previously reported to improve the catalyst performance and selectivity in the metal-free aerobic oxidations [22]. So, this idea prompted us to examine the possibility of utilizing ILs along with mesoporous magnetic MCM-41 materials in order to apply in the synthesis of valuable heterocyclic compounds such as quinazolin-4(3H)-one derivatives.

Herein, we wish to introduce the novel (α-Fe_2O_3)-MCM-41 nanocatalyst in which L-prolinium nitrate ionic liquid has been bound to the internal surface of the mesochannels of mesoporous material to give a new solid nanocatalyst which acts both as a Brønsted acid and an oxidant. This catalyst in turn showed excellent catalytic performance in direct synthesis of quinazolin-4(3H)-one derivatives **4** from isatoic anhydride **1**, primary amines **2** and an aldehyde or an aryl halide **3**, at 100 °C with good to excellent yields of the products within short reaction times (Scheme 1). We present the synthesis of quinazolin-4(3H)-one derivatives in the absence of any other extra oxidant for the first time.

2. Experimental

Melting points were recorded on a Buchi B-540 apparatus. IR spectra were recorded on an ABB Bomem Model FTLA200-100 instrument.

^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX-300 spectrometer, at 400 and 100 MHz, using TMS as an internal standard. Chemical shifts (δ) were reported relative to TMS, and coupling constants (J) were reported in hertz (Hz). Mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer with 70-eV ionization potential. X-ray powder diffraction (XRD) was carried out on a Philips X'Pert diffractometer with CuKα radiation. The pore structure of the prepared catalyst was verified by the nitrogen sorption isotherm ([5.0.0.3] Belsorp, BEL Japan, Inc.). Transmission electron micrographs (TEM) were recorded on a Philips EM-208 instrument on an accelerating voltage of 100 kV. The morphology of the catalyst and X-ray energy diffraction (XED) spectra were recorded by scanning electron microscope model VEGA\\ TESCAN-XMU instrument with an accelerating voltage of 20 kV.

2.1. Preparation of (Fe_2O_3)-MCM-41

A mixture with molar ratio of 3.2 $FeCl_3$:1.6 $FeCl_2$:1 CTABr:39NH_4OH:2300 H_2O was used for the preparation of naked Fe_3O_4 nanoparticles at room temperature. Typically, 2 g of iron (III) chloride ($FeCl_3 \cdot 6H_2O$) and 0.8 g of iron (II) chloride ($FeCl_2 \cdot 4H_2O$) were dissolved in 10 mL of distilled water under N_2 atmosphere. The resulting solution was added dropwise to a 100 mL solution of 1.0 M NH_4OH solution containing 0.4 g of cetyltrimethylammonium bromide (CTABr) to construct a colloidal suspension of iron oxide magnetic nanoparticles.

The magnetic MCM-41 was prepared by adding 20 mL of the magnetic colloid to a 1 L solution with the molar ratio of 292 NH_4OH:1 CTABr:2773 H_2O under vigorous mixing and sonication. Then sodium silicate (16 mL) was added, and the mixture was allowed to react at room temperature for 24 h under well-mixed conditions. The magnetic MCM-41 [(Fe_3O_4)-MCM-41] was filtered and washed with alcoholic ammonium nitrate. The surfactant template was then removed from the synthesized material by calcination at 450 °C for 4 h to give the [(α-Fe_2O_3)-MCM-41]. It is worth mentioning that in the absence of nitrogen the magnetic property of Fe_3O_4 is decreased.

2.2. Preparation of (α-Fe_2O_3)-MCM-41-L-prolinium nitrate

A mixture of (α-Fe_2O_3)-MCM-41 (1 g) and L-prolinium nitrate (0.71 g, 4 mmol) in 5 mL dry acetone was stirred at room temperature for 3 h, the solvent was then removed in *vacuo* and washed with CH_2Cl_2 to give (α-Fe_2O_3)-MCM-41-L-prolinium nitrate as a brown powder.

2.3. General experimental procedure for the synthesis of quinazolin-4(3H)-one derivatives in the presence of (α-Fe_2O_3)-MCM-41-L-prolinium nitrate

A mixture of isatoic anhydride (1 mmol), aldehyde or benzyl halide (1 mmol), ammonium acetate (2 mmol) or aniline derivatives (1 mmol) and the catalyst (0.03 gr) was ground thoroughly and then transferred into a reaction vessel where this mixture was stirred under 100 °C for the appropriate time. The reactions were monitored by TLC (EtOAc:Petroleum ether, 1:2). After completion of the reaction, the mixture was allowed to be cooled down to room temperature. Then chloroform (10 mL) was added and the mixture was stirred for an extra 30 min. After collecting the magnetic catalyst with an external magnet, MeOH (1 mL) was added to the chloroform solution and this solution was then concentrated in vacuo until the precipitates were formed. The products were vacuum filtered by Buchi funnel dried and recrystallized from ethanol to furnish the desired quinazolin-4(3H)-one derivative.

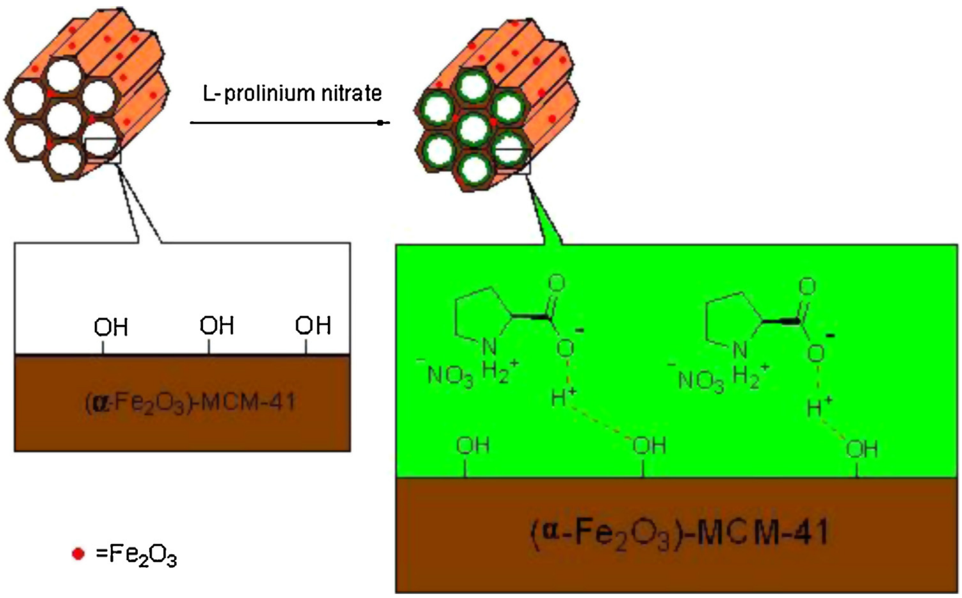
3. Results and discussions

Scheme 2 indicates the process of incorporating L-prolinium nitrate into the mesochannels of the (α-Fe_2O_3)-MCM-41 material.

The prepared catalyst (α-Fe_2O_3)-MCM-41-L-prolinium nitrate was characterized with IR, XRD, SEM, TEM, XED, nitrogen physisorption measurements, and acid–base titration. The acid–base titration showed that the pH of the catalyst is 2.69. In FT-IR spectra, the band in the region of 400–650 cm^{-1} is attributed to the stretching vibrations of the (Fe—O) bond in α-Fe_2O_3, and the band at about 1100 cm^{-1} belongs to (Si—O) stretching vibrations (Fig. 1a and c).

The broad and strong peak appeared at 2920–3388 cm^{-1} is attributed to the stretching of OH and NH_2^+ bonds and strong peaks at 1730 cm^{-1} and 1380 cm^{-1} are related to the C=O stretching bond of carboxyl group of α-amino acid nitrate salt (L-prolinium nitrate) (Fig. 1b).

The XRD pattern of the synthesized catalyst is presented in Fig. 2. The XRD analysis was performed from 2.0° (2θ) to 80.0° (2θ). XRD pattern in this region confirmed that the change of sample's color



Scheme 2. L-prolinium nitrate incorporated inside the mesochannels of (α-Fe_2O_3)-MCM-41.

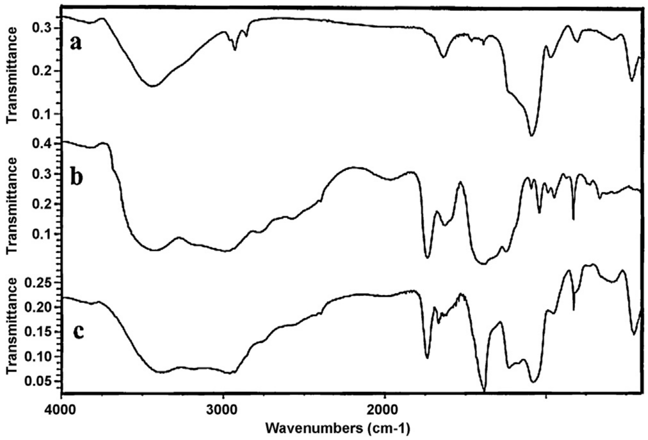


Fig. 1. The FT-IR spectra of (a) (α-Fe_2O_3)-MCM-41 (b) L-prolinium nitrate (c) (α-Fe_2O_3)-MCM-41-L-prolinium nitrate.

from black to brick-red after calcination of the catalyst is due to the oxidation of embedded Fe_3O_4 to Fe_2O_3 nanoparticles [23].

Uniform and spherical morphology of the catalyst was confirmed by SEM images (Fig. 3a and b). TEM micrograph of prepared catalyst (Fig. 3c and d) showed an ordered hexagonal pore system with embedded α-Fe_2O_3 nanoparticles.

The specific surface area, pore volume and average pore diameter were obtained by the N_2 adsorption isotherms calculated by the Brunauer–Emmett–Teller (BET) method [24] and found 1213 $m^2\,g^{-1}$, 1.59 $cm^3\,g^{-1}$ and 5.26 nm respectively before functionalization and 300 $m^2\,g^{-1}$, 0.22 $cm^3\,g^{-1}$ and 3.51 nm respectively after loading ionic liquid into the catalyst pores. The results of N_2 adsorption experiments of (α-Fe_2O_3)-MCM-41, and (α-Fe_2O_3)-MCM-41-L-prolinium nitrate are summarized in Table 1, in which the surface area, pore volume and average pore diameter of the functionalized magnetic MCM-41 were found lower than those of corresponding mesoporous silica due to loading of L-prolinium nitrate (Table 1).

The results of N_2 adsorption isotherms showed that (α-Fe_2O_3)-MCM-41filled with L-prolinium nitrate, exhibits a hysteresis loop resembling the type IV isotherm with H1-type, which is characteristic of highly ordered two-dimensional hexagonal mesostructure material with uniform open cylindrical channels and indicates that the ionic liquid was successfully introduced inside the nanochannels of (α-Fe_2O_3)-MCM-41(Fig. 4).

The X-ray energy diffraction (XED) spectra of the fresh and recovered catalyst was recorded in which no sign of degradation of the loaded ionic liquid as well as leaching of embedded nanoparticles is observed according to relative peak surfaces (Fig. 5).

After characterization of the catalyst, the reaction of isatoic anhydride **1** (1 mmol), ammonium acetate **2** (2 mmol) and 4-chlorobenzaldehyde **3b** (1 mmol), was chosen as a model reaction with various amounts of (α-Fe_2O_3)-MCM-41-L-prolinium nitrate as the catalyst at different temperature under solvent-free conditions (Scheme 3, Table 2).

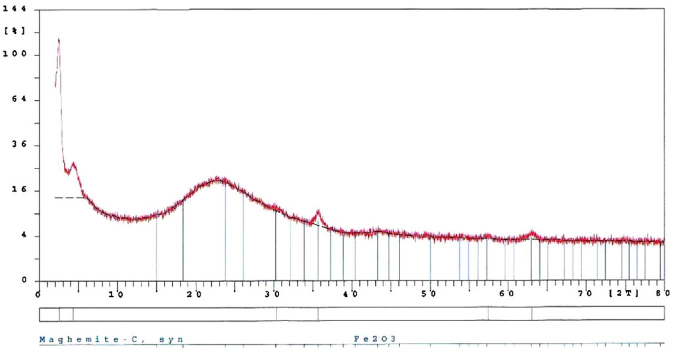


Fig. 2. The XRD patterns of the (α-Fe_2O_3)-MCM-41-L-prolinium nitrate in the region of 2.0° (2θ) to 80.0° (2θ).

Table 1
Surface area and pore volume of (Fe_2O_3)-MCM-41 and (α-Fe_2O_3)-MCM-41-L-prolinium nitrate.

Adsorbent	Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Average pore diameter (nm)
(Fe_2O_3)-MCM-41	1213	1.59	5.26
(Fe_2O_3)-MCM-L-prolinium nitrate	300	0.22	3.51

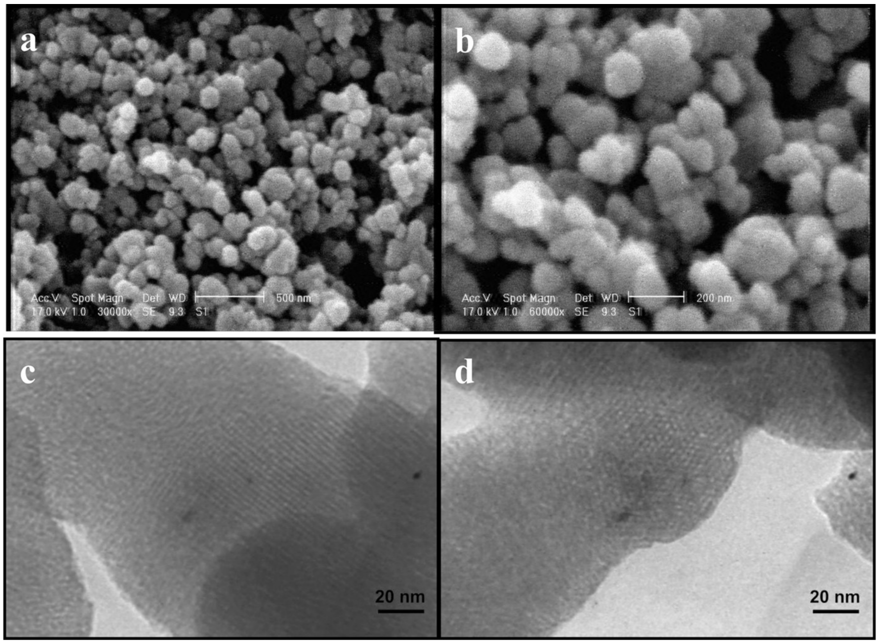


Fig. 3. (a and b) The SEM and (c and d) the TEM images of (α-Fe_2O_3)-MCM-41-L-prolinium nitrate.

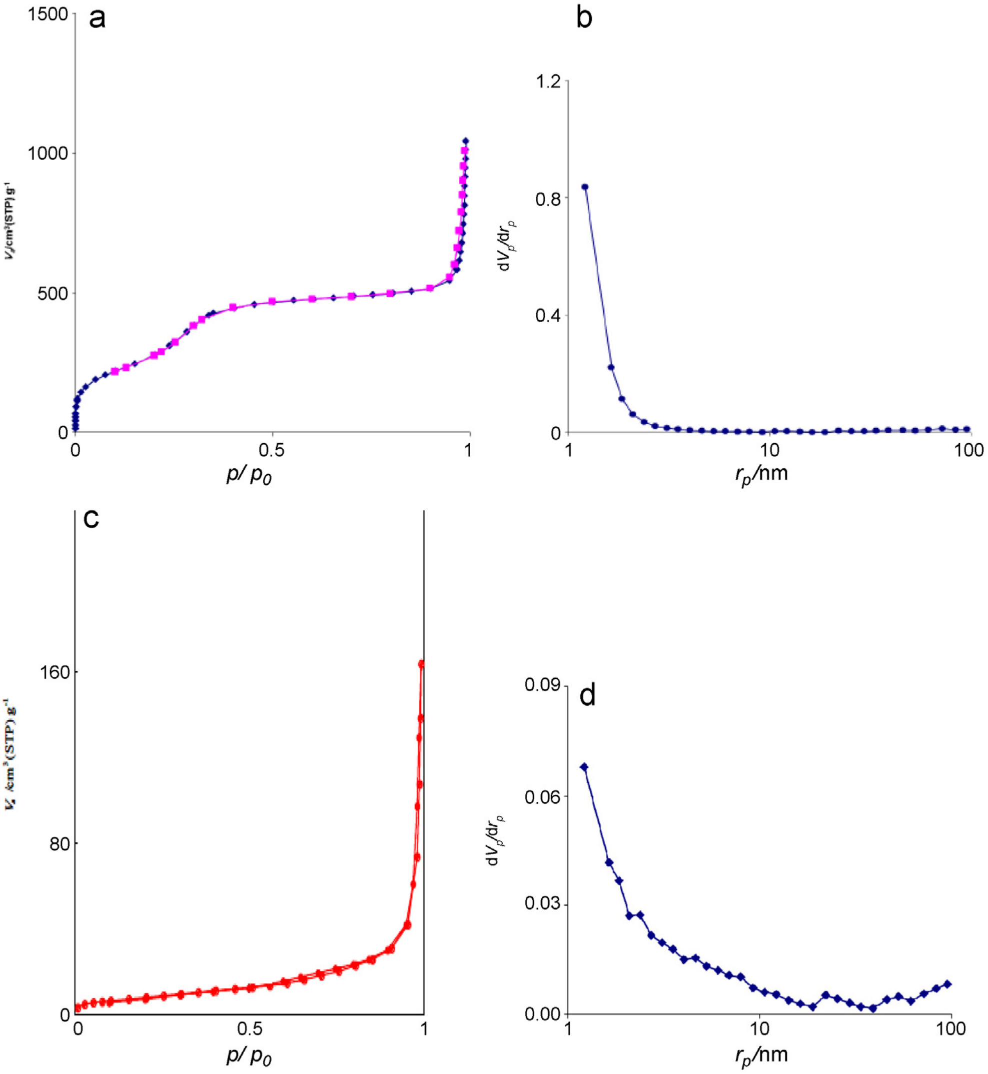


Fig. 4. Nitrogen adsorption/desorption isotherms of (a) (α-Fe_2O_3)-MCM-41 and (c) (α-Fe_2O_3)-MCM-41-L-prolinium nitrate and BJH of (b) (α-Fe_2O_3)-MCM-41 and (d) (α-Fe_2O_3)-MCM-41-L-prolinium nitrate.

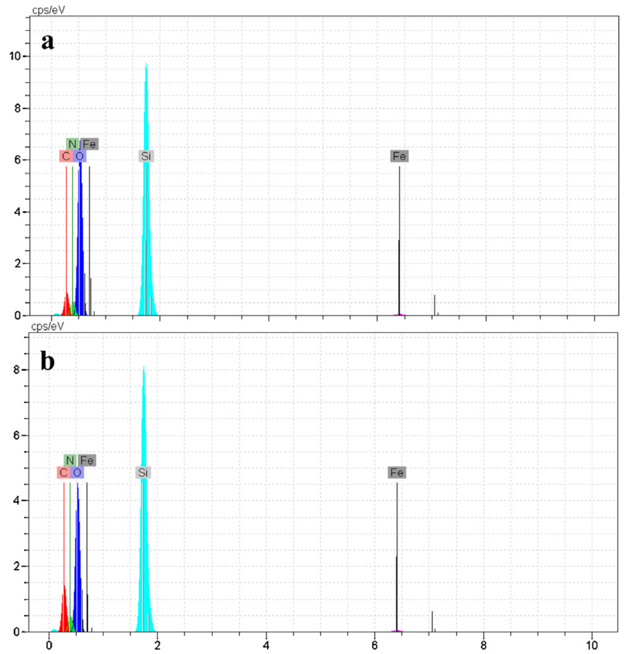


Fig. 5. The XED spectra (a) of the fresh and (b) recovered (α-Fe_2O_3)-MCM-41-L-prolinium nitrate.

Table 2
Optimization of one-pot synthesis of 2-(4-chlorophenyl)quinazolin-4(3H)-one **4b** in the presence of (α-Fe_2O_3)-MCM-41-L-prolinium nitrate as the catalyst.

Entry	(α-Fe_2O_3)-MCM-41-L-prolinium nitrate (g)	*T* (°C)	Time (min)	Yield of **4b** (%)[a]
1	0.01	rt	120	–
2	0.01	60	120	28
3	0.01	80	120	54
4	0.01	100	120	70
5	0.02	100	120	78
6	0.03	100	25	92
7	0.04	100	25	92

[a] Isolated yields.

Table 3
Investigation of the effect of the amount of L-prolinium nitrate loaded into magnetic MCM-41 channels on the reaction.

Entry	Amount of L-prolinium nitrate (mmol) loaded on 1 g of (α-Fe_2O_3)-MCM-41	Time (min)[a]	Yield (%)[b]
1	1	30	33
2	2	30	37
3	3	30	61
4	4	25	92
5	5	25	92

[a] Reactions were performed at 100 °C.
[b] Isolated yields.

Table 4
Comparison of catalytic activity of different catalysts in the model reaction.

Entry	Catalyst[a]	Time (min)[b]	Yield(%)[c]
1	MCM-41	120	62[e]
2	(α-Fe_2O_3)-MCM-41	120	75[e]
3	IL[d]-MCM-41	120	91[f]
4	IL[d]-(α-Fe_2O_3)-MCM-41	25	92[f]
5	(α-Fe_2O_3)-MCM-41-SO_3H	30	90[e]
6	L-prolinium nitrate[g]	120	28[f]

[a] 0.03 g of catalyst was used in model reaction.
[b] Model reaction was performed at 100 °C.
[c] Isolated yields.
[d] IL means L-prolinium nitrate.
[e] Non-aromatic 2,3-dihydro-2-(4-chlorophenyl)-quinazolin-4(1H)-one was obtained.
[f] Aromatic product 2-(4-chlorophenyl)quinazolin-4(3H)-one was obtained.
[g] 1 mmol of L-prolinium nitrate was used in the model reaction.

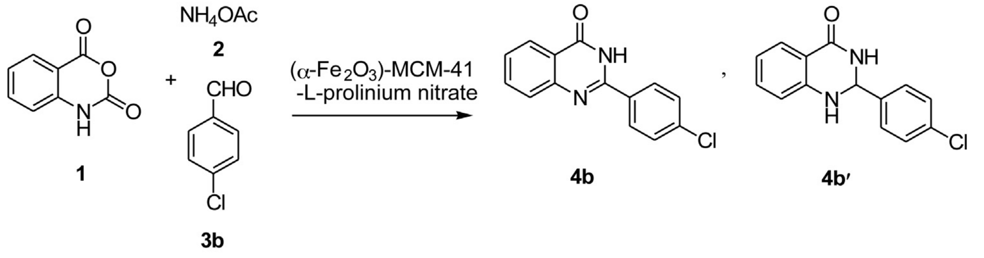
As indicated in Table 2, when 0.03 g of the catalyst was used at 100 °C, the best yield of **4b** was obtained with no sign of byproduct **4b**′ (92%, Table 2, entry 6). Further increasing of catalyst amount did affect neither the yield nor the reaction time (Table 2, entry 7).

In order to obtain suitable catalytic activity of (α-Fe_2O_3)-MCM-41-L-prolinium nitrate, we then examined different amount of L-prolinium nitrate, starting from 1 mmol to 5 mmol of IL loaded into the channels of 1 g of solid support, in which the best result was obtained in the presence of 4 mmol of L-prolinium nitrate on 1 g of (α-Fe_2O_3)-MCM-41. The results of which are shown in Table 3.

In order to compare the efficiency of this hybrid organic-inorganic catalyst with its building components, (α-Fe_2O_3)-MCM-41(not charged with L-prolinium nitrate), (α-Fe_2O_3)-MCM-41-SO_3H, MCM-41, L-prolinium nitrate -MCM-41 and L-prolinium nitrate were lonely examined under the optimized condition(Table 4).

Significant difference in the catalytic activities was clearly ascertained. Notably, the use of homogeneous L-prolinium nitrate was also shown to give considerably lower product yields (28%) (Table 4, entry 6), demonstrating the crucial role of supported ILs in obtaining high catalytic activities (Table 4, entry 4). Comparison of magnetic MCM-41 with non-magnetic MCM-41 (Table 4, entries 3 and 4), showed that the presence of ferric oxide in the solid catalyst caused the reaction to complete faster. When MCM-41, (α-Fe_2O_3)-MCM-41 and (α-Fe_2O_3)-MCM-41-SO_3H were used as catalyst in the model reaction, 2,3-dihydro-2-(4-chlorophenyl)-quinazolin-4(1H)-one were obtained as the product (Table 4, entries 1, 2 and 5) which indicates that L-prolinium nitrate has important role in the formation of aromatic product by aerobic oxidation. These observations clearly highlights the cooperative role of both IL and the solid material in promoting the reaction toward synthesis of 2-arylquinazolin-4(3H)-ones.

As summarized in Table 3, (α-Fe_2O_3)-MCM-41-L-prolinium nitrate showed significantly higher performance than either unmodified (α-Fe_2O_3)-MCM-41 or homogeneous ionic liquid L-prolinium nitrate in the synthesis of quinazolinone product.



Scheme 3. A model reaction for the optimization.

Table 5
Synthesis of 4(3H)-quinazolinone derivatives in solvent free conditions catalyzed with (α-Fe_2O_3)-MCM-41-L-prolinium nitrate.

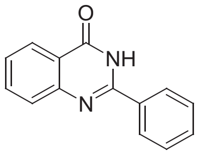
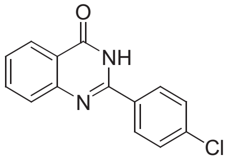
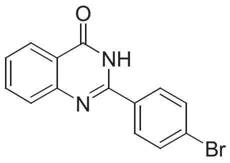
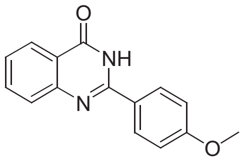
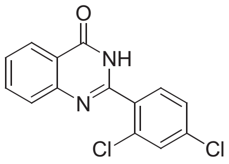
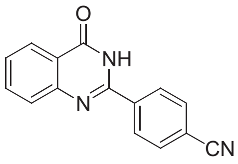
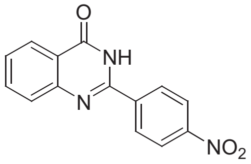
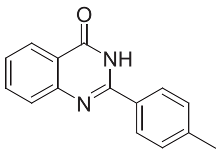
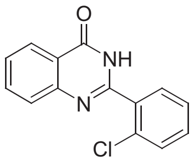
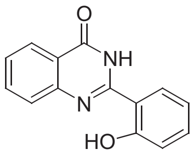
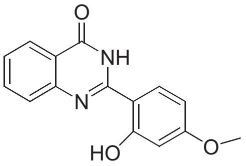
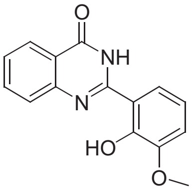
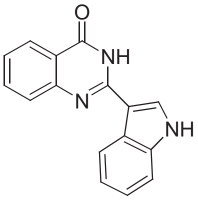
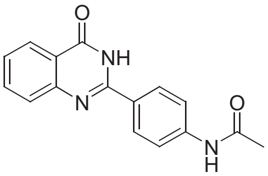
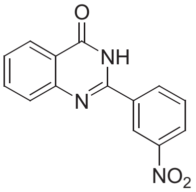
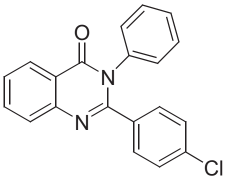
Entry		Product	Time (min.)	Yield[a)] (%)	M.P (°C) found
1	**4a**		15	97	238
2	**4b**		25	92	305
3	**4c**		15	95	318
4	**4d**		15	91	251
5	**4e**		40	84	228
6	**4f**		15	98	261
7	**4g**		25	98	363
8	**4h**		10	95	244
9	**4i**		10	97	201
10	**4j**		10	92	300

Table 5 (*Continued*)

Entry		Product	Time (min.)	Yield[a] (%)	M.P (°C) found
11	**4k**		25	90	291
12	**4l**		30	95	298
13	**4m**		25	85	290
14	**4n**		40	81	354–358
15	**4p**		40	80	353
16	**4q**		15	91	177

[a] Isolated yield.

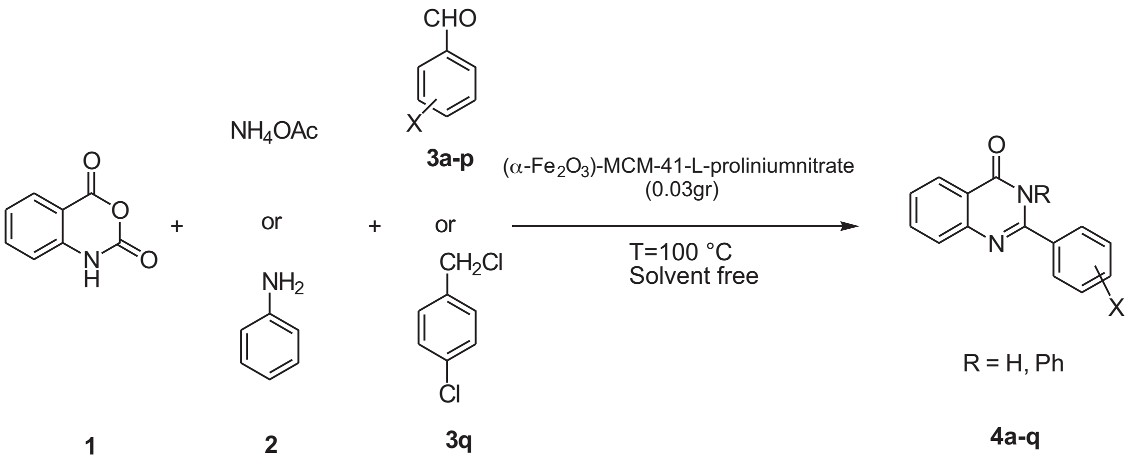
We then explored the synthesis of various quinazolin-4(3H)-one derivatives under optimized reaction conditions in order to examine the scope and generality of the process. The results are summarized in Table 5 (see Supporting Information). These results indicate the fact that the use of as low as 0.03 g of (α-Fe_2O_3)-MCM-41-L-prolinium nitrate exhibits marked efficiency on all of the aldehydes and alkyl halides tested under desired reaction conditions (Table 5, Scheme 4).

As shown in Table 5, the product **4q** was formed through the reaction between isatoic anhydride, aniline and 4-chloro-benzyl chloride in high yield, both aldehyde derivatives and alkyl halide react without any significant difference to give the corresponding quinazolin-4(3H)-ones. This reaction was fairly general, clean, rapid and efficient under the optimized reaction conditions in the presence of (α-Fe_2O_3)-MCM-41-L-prolinium nitrate.

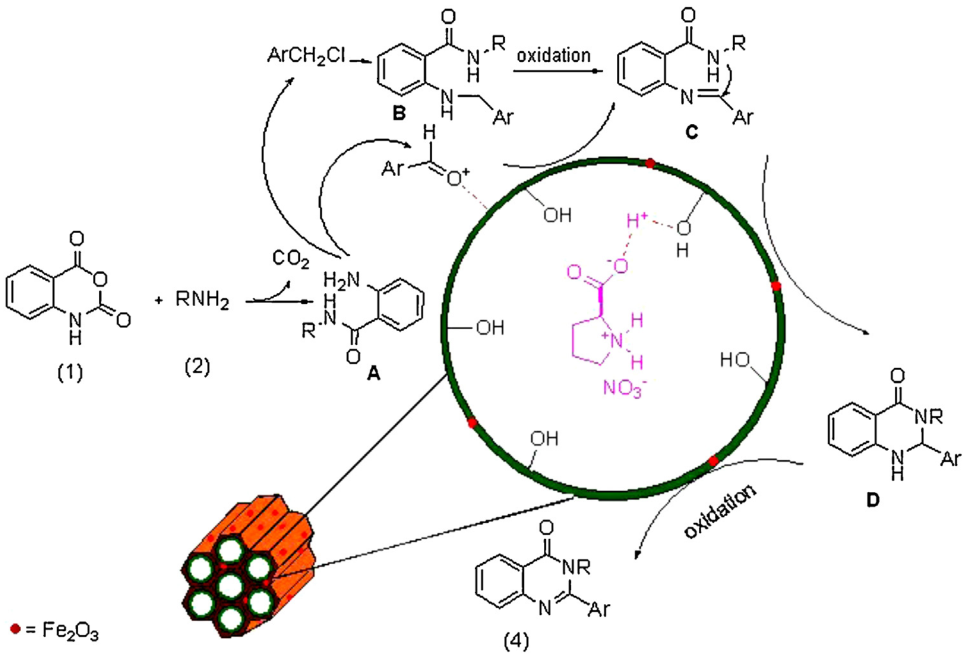
A plausible mechanism is represented in Scheme 5. The reactants easily absorb into the channels of the magnetic nanocatalyst because of its mesoporous structure and characteristic high surface area. The inherent Brönsted acidity of L-prolinium nitrate and Lewis acidity of the Fe^{3+} both contribute in the activation of carbonyl moiety in the aldehyde reactant. Afterwards, the nucleophilic addition of amine **A** to benzyl chloride and benzaldehyde lead to the formation of intermediate **B** and **C** respectively and the intermediate **B** can also be oxidized to **C** over the catalyst surface under aerobic conditions. Subsequently, the intermediate **C** undergoes intramolecular nucleophilic addition to the imine bond to form dihydroquinazolinone intermediate **D** which transforms into the desired product through oxidation under the reaction conditions.

The reusability of our new catalyst system was then examined in the model reaction under optimized reaction conditions. The results are presented in Table 6.

As can be seen, this catalytic system was recycled and reused three times with only 5% loss of reactivity (Table 6).



Scheme 4. Synthesis of quinazolin-4(3H)-one derivatives under optimized reaction conditions.



Scheme 5. A plausible mechanism for the synthesis of 4(3H)-quinazolinone derivatives in the presence of (α-Fe$_2$O$_3$)-MCM-41-L-prolinium nitrate.

Table 6
Catalytic reusability of (α-Fe$_2$O$_3$)-MCM-41-L-prolinium nitrate.

Entry	Yield of model reaction product[a] (%)
1	92
2	90
3	87

[a] Isolated yields.

4. Conclusion

In summary, we have introduced a highly powerful Brønsted solid acid catalyst that shows remarkable and somehow extraordinary catalytic activity in the synthesis of quinazolin-4(3H)-one derivatives at ambient temperature under oxidant- and solvent-free conditions in short reaction times. It is believed that the L-prolinium nitrate in the mesochannels of (α-Fe$_2$O$_3$)-MCM-41 might increase the Brønsted acid strength and oxidation power as the result of our novel cooperative catalytic system.

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Appendix A. Supplementary data

Full spectroscopic data for the synthesized quinazolinone derivatives have been provided as a separate Supporting Information. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.04.002.

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