

The Ritter reaction under incredibly green protocol: Nano magnetically silica-supported Brønsted acid catalyst

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ARTICLE INFO

Article history:

Received 16 February 2010

Received in revised form 9 June 2010

Accepted 10 June 2010

Available online 16 June 2010

Dedicated to memory of Prof. Dr. Ghaffar Motedayen Aval.

Keywords:

Functionalized silica-coated magnetic nanoparticle

Silica-supported perchloric acid

Biocompatible and recoverable catalyst

Modified Ritter reaction

ABSTRACT

HClO₄-functionalized silica-coated magnetic nanoparticles [γ -Fe₂O₃@SiO₂-HClO₄] (2.5 mol%) has been found to be a capable biocompatible and recyclable catalyst for highly efficient conversion of a variety of alcohols to corresponding amides via modified Ritter reaction in good to excellent yields. Since this heterogeneous catalyst can be simply removed by using an external magnetic device then recovered, it also enhances product purity and promises economic.

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1. Introduction

γ -Fe₂O₃ (gamma ferric oxide) is a technologically important compound widely used for the production of magnetic materials and catalysts and applied widely in magnetic storage media in audio and video recording [1–4] and biomedicine [5]. Because of the sensitivity of the magnetic nanoparticles and strong surface affinity toward silica, these nanoparticles can be directly coated with amorphous silica. There are several advantages to use silica shells instead of organic stabilizers in biomedicine application. The more important advantages of application of silica for protection the magnetic nanoparticles are: physical blocking of the surface without any affect redox reactions at the core surface; the optically transparency of silica shell that leads to modulate the position and intensity of colloidal metal surface plasmon absorption bands; the prevention of coagulation during chemical reactions [6–8].

Chakraborti and Gulhane [9] introduced a heterogeneous version of perchloric acid entitled silica-supported perchloric acid that has emerged as a powerful catalyst for various organic transformations; including synthesis of bis-indolylmethanes [10], *N*-tert-butoxycarbonylation of amines [11], selective removal of anomeric *O*-acetate groups in carbohydrates [12], cleavage of benzylidene acetals [13], glycosylation using sugar trichloroace-

timidates as glycosyl donors [14], selective deprotection of terminal isopropylidene acetals and trityl ethers [15], transformation of aldehydes to *O*-trimethyl silylated cyanides [16], esterification of carboxylic acids by alcohols [17], acetal and ketal formation and deportations [18], thia-Michael addition [19], thioacetalisation and thioketalisation [20,21]. In spite of recoverability of the silica-supported perchloric acid, the tedious recycling of catalysts by filtration and the inevitable loss of some solid catalyst in the separation process, especially with air sensitive materials, are some of the drawbacks of the traditional heterogeneous SiO₂-HClO₄. Therefore, there is more interest to introduce a novel version of HClO₄ immobilized onto magnetic silica for more efficient catalyst recovery, especially from the standpoint of green chemistry.

Due to the reasonable needs to clean and green recovery of the heterogeneous catalyst, especially acid catalyst, we decided to design a novel version of silica-supported perchloric acid to facilitate efficient recycling of this catalyst. For this purpose, we prepared the HClO₄-functionalized silica-coated magnetic nanoparticle [γ -Fe₂O₃@SiO₂-HClO₄] and after characterization, the Ritter reaction for instance selected to investigate its catalytic activity and recyclability.

The Ritter reaction is the treatment of nitriles with carbocations, generated *in situ* from alcohols or alkenes, lead to *N*-substituted amides [22]. This transformation is a very applicable and important carbon–nitrogen bond formation in organic synthesis. That is especially useful for preparation of useful amine precursors in pharmaceuticals [23]. The main disadvantage of classical Ritter

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procedure is the use of an excess amount of corrosive sulfuric acid, thus limited its applicability to compounds containing functional group stable to acid. The classical Ritter reaction is required to several modifications to overcome its limitation. Some of the modified methodologies are: $(\text{CF}_3\text{SO}_2)_2\text{O}$ [24], $\text{BF}_3\text{-OEt}_2$ [25], silica-supported $\text{Fe}(\text{ClO}_4)_3$ [26], $\text{MeSO}_3\text{H}/\text{Al}_2\text{O}_3$ [27], Nafion-H [28], $\text{CoCl}_2/\text{Ac}_2\text{O}$ [29], Fe^{3+} -K10 montmorillonite [30], heteropolyacids [31], PMA/SiO₂ [32], zeolites [33], triflic anhydride [34], $\text{P}_2\text{O}_5\text{-SiO}_2$ [35] and using tertiary esters [36] or trimethylsilyl cyanide [37] instead of alcohols or nitriles, respectively. However aforementioned developed methods suffer from the following disadvantages such as: expensive or unavailability or toxicity of the reagent, extended reaction times, additionally the main drawback of almost existing methods is that the catalysts are decomposed under aqueous work-up conditions and their recoveries are often impossible. Therefore the importance of overcoming these drawbacks is growing that as attention and many efforts are directed to develop an efficient, catalytic system for synthesis of amides, we described a green protocol recoverable and cost-effective catalyst for this purpose. In an effort we introduce a convenient and recoverable procedure for the preparation of amides from alcohols and nitriles by employing a catalytic amount of $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2\text{-HClO}_4$.

2. Experimental

2.1. Synthesis of HClO_4 -functionalized silica-coated magnetic nanoparticles $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2\text{-HClO}_4$

The maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticle was synthesized by a chemical co-precipitation technique of ferric and ferrous ions in alkali solution. $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were synthesized based on a reported method with minor modifications. $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (1.99 g) and anhydrous FeCl_3 (3.25 g) were dissolved in water (20 mL) separately, followed by the two iron salt solutions being mixed under vigorous stirring (800 rpm). A NH_4OH solution (0.6 M, 200 mL) was then added to the stirring mixture at room temperature, immediately followed by the addition of a concentrated NH_4OH solution (25%, w/w, 30 mL) to maintain the reaction pH between 11 and 12. The resulting black dispersion was continuously stirred for 1 h at room temperature and then heated to reflux for 1 h to yield a brown dispersion. The magnetic nanoparticles were then purified by a repeated centrifugation (3000–6000 rpm, 20 min), decantation, and redispersion cycle 3 times, until a stable brown magnetic dispersion (pH 9.4) was obtained.

Coating of a layer of silica on the surface of the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles was achieved by premixing (ultrasonic) a dispersion of the purified nanoparticles (8.5%, w/w, 20 mL) obtained previously with methanol (80 mL) for 1 h at 40 °C. Concentrated ammonia solution as added, and the resulting mixture was stirred at 40 °C for 30 min. Subsequently, tetraethyl orthosilicate (TEOS, 1.0 mL) was charged to the reaction vessel, and the mixture was continuously stirred at 40 °C for 24 h. The silica-coated nanoparticles were collected by a permanent magnet, followed by washing three times with EtOH, diethyl ether and drying at 100 °C in vacuum for 24 h.

HClO_4 (0.3 mmol, as a 70% aq. solution) was added to a suspension of 1 g $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2$ in Et₂O (50 mL) while dispersed by sonication. The mixture was concentrated and the residue was heated at 70 °C for 72 h under vacuum, while being mechanically stirred, to obtain $[\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2\text{-HClO}_4]$ (0.25 mmol/g, 10 mg = 0.0025 mmol of HClO_4).

2.2. Typical experimental protocol for the synthesis of amides from alcohols and nitriles

Alcohol (2 mmol) and nitrile (2.2 mmol) were mixed with $[\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2\text{-HClO}_4]$ (100 mg, 0.025 mmol, and 2.5 mol% of HClO_4)

under neat condition at room temperature, until complete disappearance of starting alcohols (as monitored by TLC). After completion, the mixture reaction diluted by 5 mL diethyl ether, then the catalytic system removed by an external magnet then mixture reaction and the organic layer was washed with aq. solution 10% NaHCO_3 and water, dried with Na_2SO_4 and concentrated to give the products. All isolated products gave satisfactory spectral data (IR, ¹H NMR and ¹³C NMR) and compared with those reported in literature.

Spectral data:

- ¹H NMR (500 MHz, CDCl_3): δ = 5.43 (brs, NH), 1.93 (s, 3H), 1.36 (s, 9H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 51.5, 29.1, 24.9.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.27–7.38 (m, 5H), 5.97 (brs, NH), 4.88–4.93 (q, 1H), 2.01 (s, 3H), 1.81–1.91 (m, 2H), 0.90–0.93 (t, 3H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 169.7, 142.5, 129, 127.7, 127, 55.3, 23.8, 11.1.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.35–7.38 (m, 4H), 7.29–7.32 (m, 2H), 7.26–7.27 (m, 4H), 6.27–6.30 (brs, 2H), 2.07 (s, 3H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 169.5, 141.9, 129, 127.89, 127.87, 57.4, 23.7.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.28–7.30 (m, 1H), 7.19–7.20 (m, 2H), 7.11–7.13 (m, 1H), 5.93–5.95 (brs, 1H), 5.18–5.19 (brs, 1H), 2.78–2.83 (m, 2H), 2.04–2.06 (m, 1H), 2.02 (s, 3H), 1.82–1.88 (m, 3H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 169.7, 137.9, 137.1, 129.5, 129.1, 127.6, 126.6, 47.8, 30.5, 29.6, 23.8, 20.3.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.20–7.32 (m, 5H), 6.23 (brs, NH), 5.05–5.11 (m, 1H), 1.92 (s, 3H), 1.44–1.45 (d, J = 6.9 Hz, 3H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 169.8, 143.8, 129, 128.9, 127.6, 126.7, 126.6, 49.2, 32.7, 22.2.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.76 (d, J = 8.03 Hz, 2H), 7.43–7.52 (m, 3H), 5.98 (brs, NH), 1.51 (s, 9H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 167.3, 136.3, 131.5, 129.0, 128.9, 127.1, 52.0, 29.3.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.81–7.82 (d, J = 7.2 Hz, 2H), 7.30–7.55 (m, 8H), 6.44 (brs, NH), 5.37–5.40 (m, 1H), 1.64–1.66 (d, J = 6.9 Hz, 3H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 167, 143.5, 135, 131.9, 129.1, 128.9, 127.9, 127.3, 126.7, 49.6, 22.1.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.86–7.87 (d, J = 7.93 Hz, 2H), 7.52–7.57 (q, 1H), 7.46–7.50 (m, 2H), 7.38–7.41 (m, 4H), 7.30–7.38 (m, 6H), 6.78–6.80 (brs, 1H), 6.50–6.51 (d, J = 7.8 Hz, 1H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 166.9, 141.9, 134.6, 132.1, 129.1, 129, 128, 127.9, 127.5, 57.8.
- ¹H NMR (500 MHz, CDCl_3): δ = 6.23–6.26 (d, J = 16.86 Hz, 1H), 6.04–6.09 (q, 1H), 5.57–5.59 (d, J = 10.19 Hz, 1H), 5.54 (brs, NH), 1.42 (s, 9H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 165.2, 132.4, 125.8, 51.7, 29.1.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.27–7.38 (m, 5H), 6.29–6.32 (d, J = 16.9 Hz, 1H), 6.13–6.18 (m, 2H), 5.64–5.66 (d, J = 10.2 Hz, 1H), 4.97–5.02 (q, 1H), 1.86–1.93 (m, 2H), 0.92–0.95 (t, 3H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 165.2, 142.4, 131.3, 129, 127.7, 127.1, 126.9, 55.4, 29.4, 11.2.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.38–7.35 (m, 4H), 7.32–7.26 (m, 6H), 6.45–6.46 (d, J = 7.31 Hz, 1H), 6.33–6.37 (m, 2H), 6.18–6.24 (q, 1H), 5.68–5.70 (d, J = 10.21 Hz, 1H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 165, 141.7, 130.9, 129.1, 127.9, 127.8, 127.6, 57.4.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.30–7.32 (d, J = 7.45 Hz, 1H), 7.20–7.24 (m, 2H), 7.13–7.15 (d, J = 7.24 Hz, 1H), 6.33–6.37 (d, J = 16.93 Hz, 1H), 6.10–6.16 (q, 1H), 5.91 (brs, NH), 5.68–5.70 (d, J = 10.28 Hz, 1H), 5.28–5.31 (m, 1H), 2.79–2.89 (m, 2H), 2.08–2.14 (m, 1H), 1.89–1.93 (m, 3H). ¹³C NMR (125.7 MHz, CDCl_3): δ = 165.1, 138, 136.9, 131.4, 129.6, 129.2, 127.7, 126.9, 126.7, 47.9, 30.4, 29.6, 20.3.
- ¹H NMR (500 MHz, CDCl_3): δ = 7.27–7.35 (m, 5H), 6.78 (brs, 1H), 6.26–6.30 (dd, J = 16.97, 1.74 Hz, 1H), 6.17–6.22 (m, 1H), 5.59–5.62 (dd, J = 16.94, 1.73 Hz, 1H), 5.19–5.22 (m, 1H),

1.50–1.52 (d, $J=6.95$ Hz, 3H). ^{13}C NMR (125.7 MHz, CDCl_3): $\delta = 165.1, 143.5, 131.3, 129, 127.7, 126.9, 126.6, 49.5, 22.1$.

3. Result and discussion

Besides aforementioned factors, the magnetic inorganic solid for instance silica-gel has been introduced as promising efficient and interesting support for immobilization of catalysts, because of its higher selectivity and activity, easier and cleaner separation and work-up subsequently recycling manner. Silica is an inert material and hence chemically and thermally stable under most of the conditions at which catalysts are operating and it can be readily separated from the reaction mixture. However, a wide range of different experimental conditions has been reported in literatures for obtaining pure $\gamma\text{-Fe}_2\text{O}_3$ phase nanoparticles in the silica matrix [38–42]. In these heterogeneous reactions, catalysts were recovered by tedious procedures such as centrifugation and filtration and lead to loss of solid catalyst in the separation process. Magnetic separation provides an easy and convenient method for removing and recycling magnetized species by applying an appropriate magnetic field. In this paper, we have described the preparation of perchloric acid supported on silica-coated $\gamma\text{-Fe}_2\text{O}_3$ as a magnetized species of perchloric acid and its potential application in the synthesis of amides via Ritter reaction.

Firstly, silica-coated ultrafine and uniform $\gamma\text{-Fe}_2\text{O}_3$ core-shell particles were synthesized. The maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticle was synthesized by a chemical co-precipitation technique of ferric and ferrous ions in alkali solution. $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were synthesized based on a reported method with minor modifications [43]. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and anhydrous FeCl_3 were dissolved in water separately, followed by the two iron salt solutions being mixed under vigorous stirring (700 rpm). Then a NH_4OH solution was added to the stirring mixture at room temperature, immediately followed by the addition of a concentrated NH_4OH solution to maintain the reaction pH between 11 and 12. The resulting black



Fig. 1. Schematic synthesis of $\gamma\text{-Fe}_2\text{O}_3@SiO_2$.

dispersion was continuously stirred for 1 h at room temperature and then heated to reflux for 1 h to yield a brown dispersion. The magnetic nanoparticles were then purified by a repeated centrifugation, decantation and redispersion cycle 3 times, until a stable brown magnetic dispersion (pH 9.4) was obtained. Coating of a layer of silica on the surface of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles was achieved by premixing (ultrasonic) a dispersion of the purified nanoparticles obtained previously with methanol for 1 h at 40°C . Subsequently, tetraethyl orthosilicate (TEOS) was charged to the reaction vessel and the mixture was continuously stirred at 40°C for 24 h. The silica-coated nanoparticles were collected by a permanent magnet, followed by washing three times with ethanol, diethyl ether and then drying at 100°C in vacuum for 24 h (Fig. 1).

HClO_4 was added to a suspension of 1 g [$\gamma\text{-Fe}_2\text{O}_3@SiO_2$] in Et_2O (50 mL) while swirling. The mixture was concentrated and the residue was heated at 70°C for 72 h under vacuum, to obtain [$\gamma\text{-Fe}_2\text{O}_3@SiO_2\text{-HClO}_4$], the loading of HClO_4 measured by back titration and pH analysis (0.25 mmol/g, 10 mg = 0.0025 mmol of HClO_4). [$\gamma\text{-Fe}_2\text{O}_3@SiO_2\text{-HClO}_4$] Nanocrystallites were characterized by IR, TEM, SEM and XRD. In the TEM and SEM (Fig. 2a–c) and IR spectra (Fig. 2e) for [$\gamma\text{-Fe}_2\text{O}_3@SiO_2\text{-HClO}_4$] are presented. In the case of $\gamma\text{-Fe}_2\text{O}_3$, the band from $400\text{--}650\text{ cm}^{-1}$ is assigned to the stretching vibrations of (Fe–O) bond in γ -phase Fe_2O_3 , and the band at about 1100 cm^{-1} is ascribed to stretch of (Si–O) bond. Amorphous $\gamma\text{-Fe}_2\text{O}_3@SiO_2$ is subjected to further structural characterization with XRD (Fig. 2d). Diffraction peaks at around $35.5^\circ, 43.1^\circ, 62.8^\circ, 54^\circ$ corresponding to the (3 1 1), (4 0 0), (5 1 1)

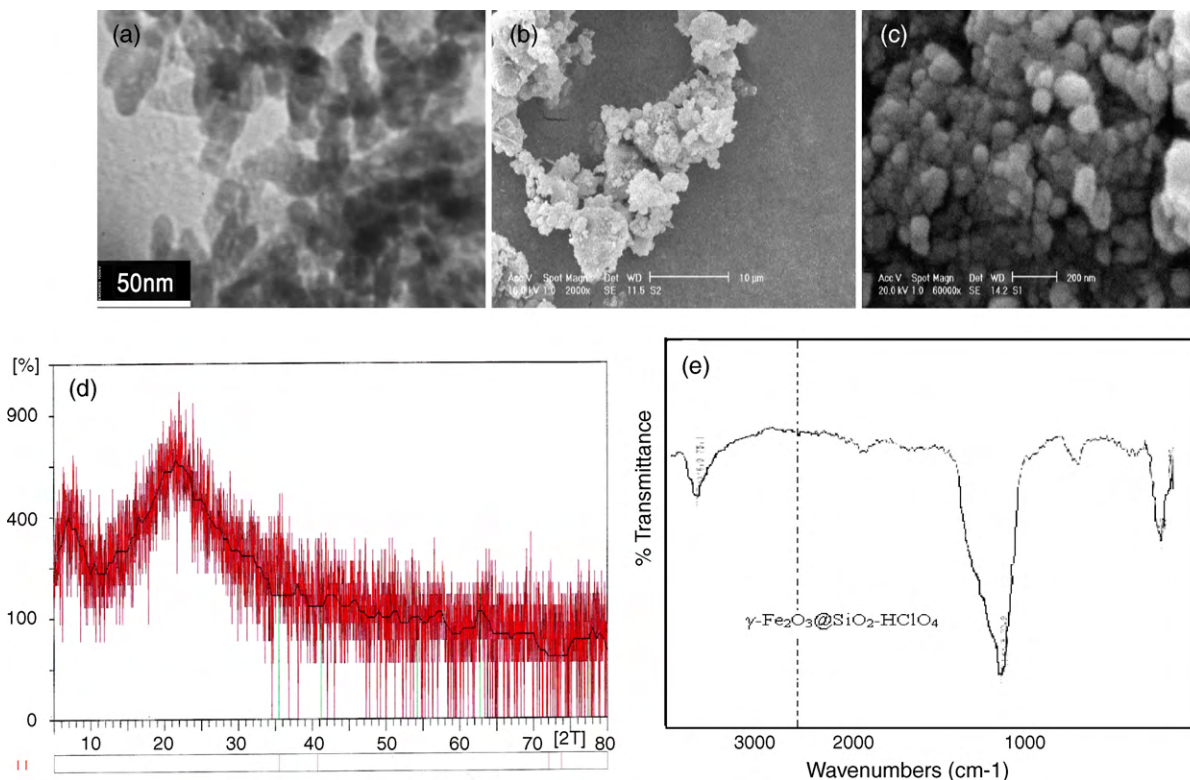


Fig. 2. The TEM (a), SEM (b and c), XRD spectra (d) and the IR spectra (e) of [$\gamma\text{-Fe}_2\text{O}_3@SiO_2\text{-HClO}_4$].

Table 1The reaction was carried out in below condition: alcohol:nitrile:cat [γ -Fe₂O₃@SiO₂-HClO₄] in respectively 1 equiv.:1.5 equiv.:2.5 mol%.


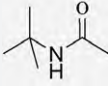
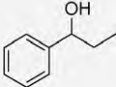
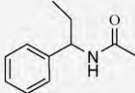
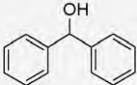
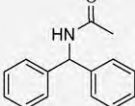


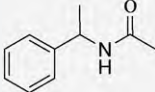


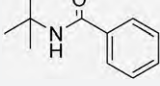

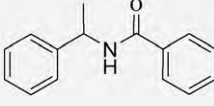
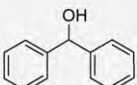



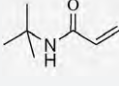

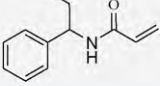
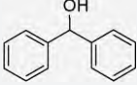



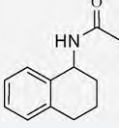


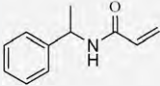
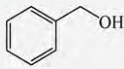
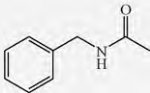
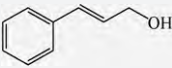
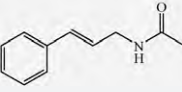
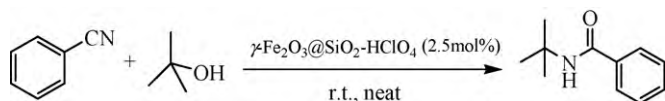
Entry	Alcohol	Nitrile	Time (h)	Product	Yield (%)
1		CH ₃ CN	4		94
2		CH ₃ CN	4		95
3		CH ₃ CN	5		95
4		CH ₃ CN	5		94
5		CH ₃ CN	4		96
6			5		97
7			3		97
8			4.5		95
9			4		92
10			4		94
11			5		93
12			6		92
13			5		90

Table 1 (Continued)

Entry	Alcohol	Nitrile	Time (h)	Product	Yield (%)
14		CH ₃ CN	4		92
15		CH ₃ CN	4		91



Scheme 1. *N*-substituted amides synthesized via Ritter reaction in the presence of $\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2\text{-HClO}_4$.

and (440) are readily recognized from the XRD pattern. The observed diffraction peaks agree well with the tetragonal structure of maghemite (1999 JCPDS file no. 13-0458).

Initially in order to investigate the catalytic activity of [$\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2\text{-HClO}_4$] in Ritter reaction, we examined its efficiency in a model reaction between benzonitrile (1.5 equiv.) and *tert*-butanol (1.0 equiv.) under neat condition at r.t. to give the corresponding *N*-substituted amide in 97% yield (Scheme 1). After some efforts a catalytic amount of [$\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2\text{-HClO}_4$] (2.5 mol% of HClO₄) was found superior for this functional transformation. Encouraged by the result, we decided to generalize this new protocol by subjecting various substituted alcohols and nitriles. By using the same condition, a series of *N*-substituted amides were prepared in high yields. This method is extendable to allylic alcohol such as cinammyl alcohol and benzyl alcohol. But primary alcohols did not carried out this reaction in the present of magnetic nanoparticles $\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2\text{-HClO}_4$ (2.5 mol%) and lead to other products. The results and efficiency of the present protocol are summarized in Table 1.

Our examination showed that this method is applicable and mild for synthesis of various amides from secondary and tertiary alcohols in good to excellent yields. Interestingly, the magnetic property of [$\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2\text{-HClO}_4$] facilitates efficient recovery from the reaction mixture during the work-up procedure by an external magnet and washed the catalyst by organic solvent (Et₂O), then drying 30 min at 110 °C to ready for later run. The percentage of the recovery step in most cases was more than 98%. Moreover the recovered catalyst was recycling in subsequent runs without observation significant decrease in activity even after four runs. For example the reaction of *tert*-butanol and benzonitrile gave *N*-*tert*-butyl benzamide in sequenced six runs (Fig. 3).

This undoubtedly renders the above protocol as an economically and environmentally benign procedure for synthesis of amides from alcohols. To determine the percent leaching of the acid, the

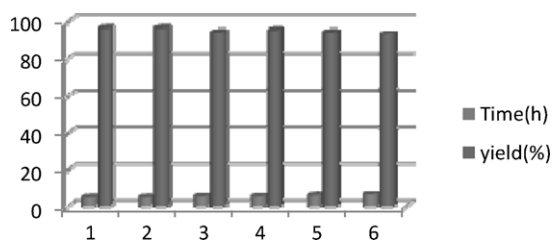
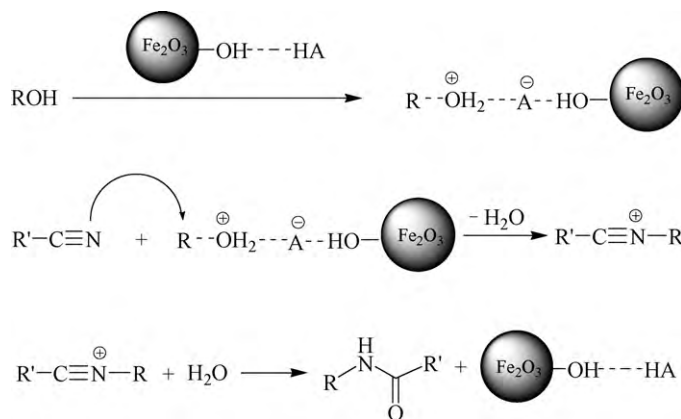


Fig. 3. The recovery of $\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2\text{-HClO}_4$ in the Ritter reaction between benzonitrile and *tert*-butanol.



Scheme 2. Proposed mechanism of reaction.

reaction of *tert*-butanol and benzonitrile gave *N*-*tert*-butyl benzamide was carried out in the presence of [$\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2\text{-HClO}_4$] for 2 h and at that point the catalyst was separated by external magnet. The residue was then allowed to react, but no significant progress was observed after 6 h. The proposed mechanism is shown in Scheme 2.

In conclusion, we have developed a simple and efficient magnetically recyclable and efficient nanocomposite catalyst for the preparation of various amides from alcohols and nitriles using the [$\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2\text{-HClO}_4$] as catalyst. The most important achievements in our efforts have present as new, mild, cost-effective and applicable efficient reusable catalytic system for modified Ritter reaction. We expect this magnetic nanocomposite catalyst system to find applications in many other industrially important catalytic processes.

Acknowledgments

We would like to express our sincere thanks to Professor Mohamed Yalpani for his helpful discussion.

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