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Silica coated magnetic $NiFe_2O_4$ nanoparticle supported phosphomolybdic acid; synthesis, preparation and its application as a heterogeneous and recyclable catalyst for the one-pot synthesis of tri- and tetra-substituted imidazoles under solvent free conditions†

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In this research, a magnetically-recoverable catalyst ($NiFe_2O_4@SiO_2–H_3PMo_{12}O_{40}$) was prepared by supporting phosphomolybdic acid ($H_3PMo_{12}O_{40}$) onto silica-coated $NiFe_2O_4$ nanoparticles. The prepared sample was characterized by FT-IR, TEM, SEM and VSM techniques and then the catalytic activity of this catalyst was investigated in the synthesis of tri- and tetra-substituted imidazole derivatives. More importantly, the catalyst was easily isolated from the reaction mixture by a magnetic bar and reused at least ten times without significant degradation in its activity.

Introduction

Magnetic nanoparticles (MNPs) have captured much attention as attractive solid supports for the immobilization of homogeneous catalysts.[1] This is because MNPs can be well dispersed in reaction mixtures without any magnetic field, providing a large surface area to be readily accessible to substrate molecules. Moreover, after completing the reactions, MNP supported catalysts can be efficiently isolated from the product solution through a simple magnetic separation process.[2,3]

Ni–Fe ferrites are some of the most versatile magnetic materials as they have a high saturation magnetization, high Curie temperature, chemical stability and relatively high permeability.[4] Phosphomolybdic acid (PMA) belongs to a class of heteropolyacids (HPAs). HPAs are commercially cheap and environmentally friendly catalysts. They exhibit high activities and selectivities and allow cleaner processes than conventional catalysts. Supported HPAs on silica-coated Ni–Fe ferrite MNPs can produce heterogeneous catalytic systems that possess both a high separation efficiency and a relatively high surface area to maximize the catalyst loading and activity.[5,6]

The development of a simple, well-organized, and environmentally synthetic method for broadly used organic compounds from readily available reagents is one of the major challenges for chemists.[7] With a wide range of applications, imidazoles have been receiving growing attention in recent years.[8] The imidazole core is present in many molecules with biological activities such as being anti-allergenic,[9] anti-inflammatory,[10] analgesic, antifungal, antimycotic, antibiotic, anti-ulcerative, antibacterial and antitumoral.[11] Plus, being known as inhibitors of p38 MAP kinases[12] and therapeutic agents, various substituted imidazoles also act as plant growth regulators, glucagon receptors,[13] photosensitive compounds in photography, and building blocks for the synthesis of other classes of compounds.[14] Among them, tri- and tetrasubstituted imidazoles have received much attention recently.[15] In the last decades, many methods have been developed for the synthesis of tri- and tetrasubstituted imidazoles by the reaction of aldehydes, and benzil or benzoin with (i) ammonium acetate, and (ii) ammonium acetate and amines in the presence of various reagents or catalysts such as: $BF_3–SiO_2$,[16] silica gel–$NaHSO_4$,[17] $HClO_4–SiO_2$,[18] $K_5CoW_{12}O_{40}\cdot 3H_2O$,[19] $InCl_3\cdot 3H_2O$,[20] L-proline,[21] I_2,[22] zeolite-HY–$Cu(NO_3)_2$,[23] MCM-41 or *p*-TsOH,[24] 1-butyl-3-methylimidazolium bromide [Bmim]Br,[25] poly(AMPS-*co*-AA),[26] 1,3-disulfonic acid imidazolium hydrogen sulfate [Dsim][HSO_4],[27] nano-crystalline sulfated zirconia (SZ),[28] 1-ethyl-3-methylimidazolium acetate [Emim][OAc],[29] [Et_3NSO_3H]Cl,[30] 1,1,3,3-*N*,*N*,*N*′,*N*′-tetramethylguanidinium trifluoroacetate (TMGT),[31] DABCO,[32] acetic acid,[33] silica-bonded propylpiperazine *N*-sulfamic acid (SBPPSA),[34] silica chloride,[35] europium

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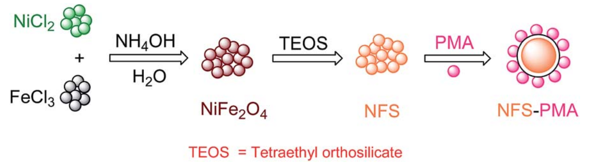
triflate [Eu(OTf)$_3$],[36] *p*-dodecylbenzenesulfonic acid (DBSA),[37] trichloroisocyanuric acid (TCCA),[38] tetrabutyl ammonium bromide (TBABr),[39] 1-methylimidazolium trifluoroacetate ([Hmim]TFA),[40] and without any catalyst.[41] Many of the synthetic methods for imidazoles suffer from one or more disadvantages such as low yields, harsh reaction conditions, difficult work-up, prolonged time period and the application of hazardous and expensive catalysts. Hence the development of clean, high yielding, and environmentally benign approaches is still desirable and much in demand. In this full paper, we report our efforts and success in developing an effective one-pot multi-component reaction of aldehydes and benzil or benzoin with (i) ammonium acetate, and (ii) ammonium acetate and amines in the presence of magnetic supported catalyst ($NiFe_2O_4@SiO_2$–$H_3PMo_{12}O_{40}$ designed NFS–PMA).

Results and discussion

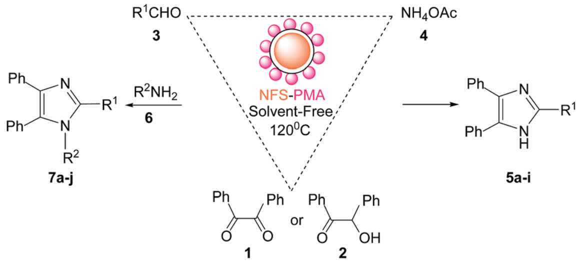
The heterogenization of HPAs on silica coated nanomagnetic materials has been an interesting approach during the past years. This strategy enabled research groups to overcome the limitations involved in the separation and recycling of homogeneous catalysts.[42] Thus, in this study, an efficient magnetic supported acid catalyst (NFS–PMA) was prepared by the chemical supporting of Keggin HPAs onto silica coated $NiFe_2O_4$ MNPs (Scheme 1).

In the continuation of our efforts toward the development of greener methodologies,[43] we now report that $NiFe_2O_4@SiO_2$–$H_3PMo_{12}O_{40}$ is a green catalyst for the synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles (Scheme 2).

In order to determine the properties of this acidic supported nanomagnetic catalyst, it was characterized by various techniques such as FT-IR (Fig. 1), SEM and TEM (Fig. 2), particle size dispersion (Fig. 3) and VSM (Fig. 4). The FT-IR spectra of NFS, PMA and NFS–PMA are compared in Fig. 1. The FT-IR spectrum of NFS (Fig. 1a) exhibits high intense absorption peaks at 1200 cm^{-1} and 1100 cm^{-1} and these peaks are assigned to the longitudinal and transverse stretching vibration modes of the Si–O–Si asymmetric bond, respectively. Additional bands at 812 cm^{-1} and 470 cm^{-1} are also identified as characteristic peaks of the Si–O–Si bond. The other peak observed at 950 cm^{-1} assigned to the SiO_3^{2-} vibrations indicates the existence of non bridging oxygen ions.[44] The spectrum of PMA (Fig. 1b) shows determined bands for absorptions at 1064 (P–O), 962 (Mo═O), 882 and 767 (Mo–O–Mo) cm^{-1}.[45] The last FT-IR spectrum (Fig. 1c) corresponds to NFS–PMA, the characteristic bands at 963, 880 and 765 cm^{-1} confirm that the PMA was well supported on the surface of NFS.



Scheme 1 Preparation of $NiFe_2O_4@SiO_2$–$H_3PMo_{12}O_{40}$ (NFS–PMA).



Scheme 2 Synthesis of 2,4,5-trisubstituted imidazoles and 1,2,4,5-tetrasubstituted imidazoles.

The morphological features and distribution of the NFS MNPs were investigated by the TEM and SEM techniques (Fig. 2a and b). The TEM and SEM photographs demonstrate that the NFS MNPs are narrowly distributed, well dispersed and are also almost spherical with a regular shape. Also, the particle size dispersion diagram (Fig. 3) from the NFS NPs shows that these MNPs have a size between 25 and 97 nm and the mean diameter is 53 nm.

The great importance of core/shell materials lies within their sufficient magnetic and superparamagnetic properties. Magnetic hysteresis measurements for $NiFe_2O_4$ were done in an applied magnetic field at r.t., with the field sweeping from −10 000 to +10 000 Oersted. As shown in Fig. 4, the $M(H)$ hysteresis loop of the samples was completely reversible, showing that the nanoparticles exhibit superparamagnetic characteristics. The hysteresis loop reached saturation up to the maximum applied magnetic field. The magnetic saturation values of $NiFe_2O_4$ are 16.71 emu g^{-1} at r.t. These MNPs showed high permeability in magnetization and their magnetization was sufficient for magnetic separation with a conventional magnet.

Our initial attempt started with the reaction of benzaldehyde (1 mmol), benzil (1 mmol), and ammonium acetate (7 mmol) in the presence of $NiFe_2O_4@SiO_2$–$H_3PMo_{12}O_{40}$ (NFS–PMA) under

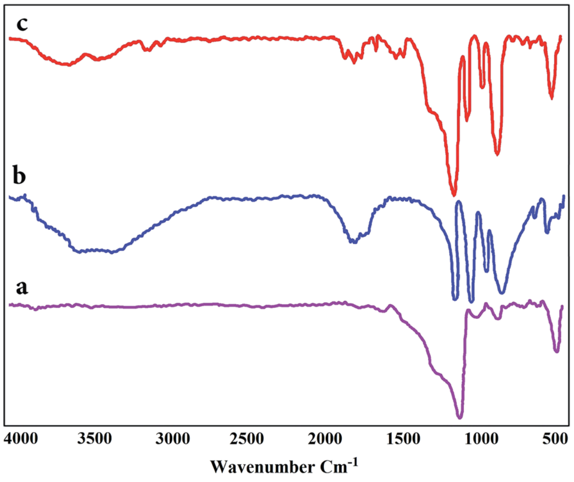


Fig. 1 FT-IR spectra of (a) $NiFe_2O_4@SiO_2$ (NFS), (b) $H_3PMo_{12}O_{40}$ (PMA) and (c) $NiFe_2O_4@SiO_2$–$H_3PMo_{12}O_{40}$ (NFS–PMA).

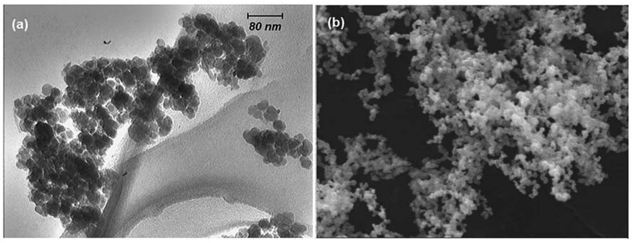


Fig. 2 (a) TEM and (b) SEM images of $NiFe_2O_4@SiO_2$ (NFS).

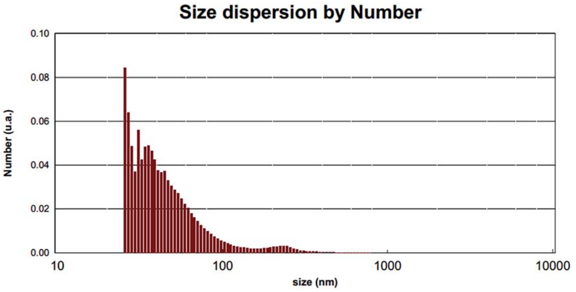


Fig. 3 Particle size dispersion of $NiFe_2O_4@SiO_2$ (NFS).

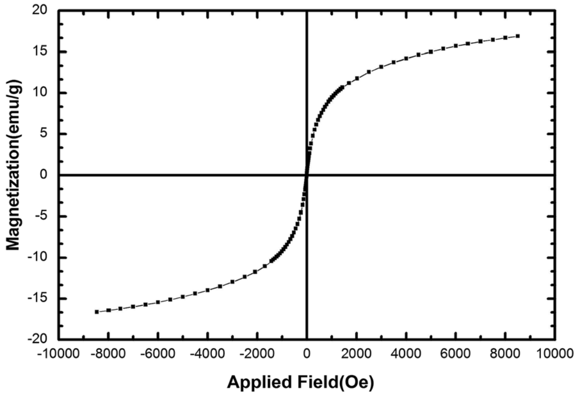


Fig. 4 Vibrating sample magnetometer (VSM) curve of $NiFe_2O_4$ at room temperature.

solvent free conditions at 120 °C (Table 1, entry 1). Then, the effect of various temperatures were investigated, and 120 °C was the optimal temperature (entries 2 and 3). Additionally, this reaction took place using various amounts of catalyst at 120 °C (entries 4 and 5). The yields were reduced in the presence of $H_3PW_{12}O_{40}$ and SiO_2 under similar conditions (entries 6 and 7). In the absence of a catalyst, the yield was trace (entry 8).

The optimal conditions were then applied for the preparation of a series of 2,4,5-trisubstituted imidazoles. The product yields are shown in Table 2. In each case, no side product formation was observed, as is normally the case in such reactions under the influence of strong acids. This method not only affords the products in excellent yields but also avoids the problems associated with catalyst cost, handling, safety, and pollution. The use of benzoin in place of benzil also gave similar results, as shown in Table 2. Encouraged by this success, a study on the synthesis of 1,2,4,5-tetrasubstituted imidazoles from benzil or benzoin, amine, ammonium acetate and various aromatic aldehydes was carried out (Table 2).

In order to illustrate the efficiency of our procedure, the results for the preparation of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles previously reported are compared with our data (Table 3). The present method using $NiFe_2O_4@SiO_2–H_3PMo_{12}O_{40}$ (NFS–PMA) as the catalyst offers several advantages such as excellent yields, a simple procedure, short reaction times, facile work-up and greener conditions.

A plausible mechanism of the reaction is presented in Scheme 3.

To determine the applicability of catalyst recovery, at the end of the reaction, with the aid of an external magnet, the catalyst was held on the side wall of the reaction vessel, while the solution was decanted. The catalyst was washed with chloroform to remove residual product, dried at 100 °C under vacuum and reused in a subsequent reaction with excellent yields. It showed the same activity as the fresh catalyst without any significant loss of its activity (Fig. 5).

Experimental Section

All reagents were purchased from Merck and Sigma-Aldrich and used without further purification. IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer (KBr pellets). ^1H NMR spectra were obtained using Bruker 250 and 300 MHz spectrometers in DMSO-d_6 or $CDCl_3$ and using TMS as the internal reference. Melting points were determined in open capillary tubes in a Stuart BI Branstead Electrothermal cat no. IA9200 apparatus and uncorrected. The particle size and morphology of the synthesized catalyst were characterized with a transmission electron microscope (TEM) (Philips CM-200 and Titan Krios) and scanning electron microscope (SEM) (Philips XL 30 and S-4160) with gold coating. The size dispersion of the samples was obtained using a laser particle size analyzer (CORDOUAN, Vasco3).

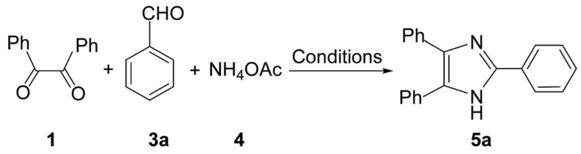
Preparation of the catalyst

The silica coated $NiFe_2O_4$ MNPs (NFS, Scheme 1) were synthesized according to our previous reports[46–48] and then, for the immobilization of PMA on NFS, 0.5 g of PMA was dissolved in 5 mL of methanol.[49] This solution was added dropwise to a suspension of 1.0 g NFS in methanol (50 mL) and then the mixture was heated at 70 °C for 48 h under vacuum while being mechanically stirred and gave the supported nanomagnetic catalyst (NFS–PMA). The catalyst was collected by a permanent magnet and dried under vacuum overnight and after the first drying, the supported nanocatalyst was calcined at 250 °C for 2 h.[50,51]

General procedure for the synthesis of 2,4,5-trisubstituted imidazoles (5a–i)

A mixture of benzil or benzoin (1 mmol), aldehyde (1 mmol), ammonium acetate (7 mmol) and NFS–PMA (0.02 g) was

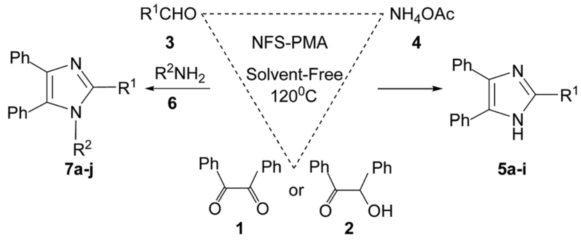
Table 1 Screening of the reaction conditions for the synthesis of 2,4,5-triphenyl-imidazole (**5a**)



Entry	Amount of catalyst (g)	Conditions	Time (min)	Yield[a] (%)
1	NFS–PMA (0.02 g)	Solvent-free/120 °C	20	94
2	NFS–PMA (0.02 g)	Solvent-free/110 °C	20	87
3	NFS–PMA (0.02 g)	Solvent-free/130 °C	20	92
4	NFS–PMA (0.03 g)	Solvent-free/120 °C	20	92
5	NFS–PMA (0.01 g)	Solvent-free/120 °C	30	89
6	PMA (0.03 g)	Solvent-free/120 °C	20	72
7	SiO_2 (0.03 g)	Solvent-free/120 °C	20	Trace
8	—	Solvent-free/120 °C	20	Trace

[a] Isolated yields.

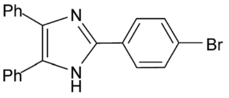
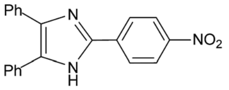
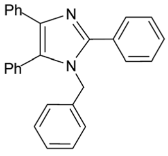
Table 2 Three and four component synthesis of the 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles from the reaction of aldehydes, and benzil or benzoin with (i) ammonium acetate, and (ii) ammonium acetate and amines in the presence of $NiFe_2O_4@SiO_2–H_3PMo_{12}O_{40}$ (NFS–PMA)[a]



Products (**5**,**7**)	R^1	R^2	Time (min)		Yields[b] (%)		Ref.
			Benzil	Benzoin	Benzil	Benzoin	
5a	C_6H_5	—	20	20	94	90	21
5b	$4\text{-}BrC_6H_4$	—	10	15	96	82	28
5c	$3\text{-}NO_2C_6H_4$	—	20	20	93	91	21
5d	$3\text{-}OHC_6H_4$	—	10	10	96	94	21
5e	$4\text{-}NO_2C_6H_4$	—	20	25	90	90	21
5f	$4\text{-}CH_3C_6H_4$	—	15	15	92	90	21
5g	$4\text{-}OCH_3C_6H_4$	—	20	20	90	90	21
5h	2-Thienyl	—	20	25	91	88	41
5i	2-Furyl	—	25	30	87	86	41
7a	C_6H_5	$PhCH_2$	25	30	88	86	18
7b	$4\text{-}BrC_6H_4$	$PhCH_2$	15	15	87	81	18
7c	$4\text{-}CH_3C_6H_4$	$PhCH_2$	15	15	90	90	18
7d	$3\text{-}OHC_6H_4$	$PhCH_2$	15	20	89	87	34
7e	$4\text{-}OCH_3C_6H_4$	$PhCH_2$	20	20	88	87	18
7f	2-Thienyl	2-Thienyl CH_2	20	25	84	82	15*b*
7g	C_6H_5	$3,4\text{-}OMeC_6H_4CH_2$	10	15	90	86	15*b*
7h	C_6H_5	$PhNH_2$	35	40	84	80	16
7i	$4\text{-}BrC_6H_4$	$PhNH_2$	25	30	85	80	28
7j	$4\text{-}N(CH_3)_2C_6H_4$	$3\text{-}NO_2C_6H_4$	30	30	78	75	18

[a] All known products have been reported previously in the literature and were characterized by comparing the IR and NMR spectra with authentic samples. [b] Isolated yields.

Table 3 Comparison of methods for the synthesis of 2,4,5-trisubstituted imidazoles and 1,2,4,5-tetrasubstituted imidazoles

Entry	Compounds	Conditions	Time (min)	Yield (%)
1	 **5b**	Present work	10	96
		InCl$_3$·3H$_2$O/MeOH/rt[20]	540	76
		Nano-crystalline sulfated zirconia (SZ)/EtOH/reflux[28]	75	81
		[Et$_3$NSO$_3$H]Cl/solvent-free/100 °C[30]	120	87
		DABCO/*t*-BuOH/60–65 °C[32]	720	82
		Silica chloride/solvent-free/80 °C[35]	30	84
		p-Dodecylbenzenesulfonic acid/H$_2$O/reflux[37]	240	75
		TCCA/EtOH/reflux[38]	720	90
		TBABr/*t*-BuOH/80 °C[39]	480	88
		[Hmim][TFA]/H$_2$O/80 °C[40]	50	91
		Catalyst-free/MeOH/60 °C[41]	240	90
2	 **5e**	Present work	20	90
		InCl$_3$·3H$_2$O/MeOH/rt[20]	500	76
		Nano-crystalline sulfated zirconia (SZ)/EtOH/reflux[28]	70	80
		[EMIM]OAc/EtOH/ultrasonic/rt[29]	70	70
		[Et$_3$NSO$_3$H]Cl/solvent-free/100 °C[30]	100	92
		TMGT/solvent-free/100 °C[31]	20	84
		DABCO/*t*-BuOH/60–65 °C[32]	720	89
		Silica chloride/solvent-free/80 °C[35]	30	78
		p-Dodecylbenzenesulfonic acid/H$_2$O/reflux[37]	240	81
		TCCA/EtOH/reflux[38]	720	95
		TBABr/*t*-BuOH/80 °C[39]	420	83
		[Hmim][TFA]/H$_2$O/80 °C[40]	30	91
		Catalyst-free/MeOH/60 °C[41]	240	86
3	 **7a**	Present work	25	88
		BF$_3$–SiO$_2$/solvent-free/140 °C[16]	120	80
		K$_5$CoW$_{12}$O$_{40}$·3H$_2$O/solvent-free/140 °C[19]	120	90
		InCl$_3$·3H$_2$O/MeOH/rt[20]	520	51
		L-Proline/MeOH/60 °C[21]	540	86
		p-TsOH/solvent-free/140 °C[24]	115	79
		[Bmim]Br/solvent-free/140 °C[25]	120	90
		Poly(AMPS-*co*-AA)/solvent-free/110 °C[26]	30	87
		[Dsim][HSO$_4$]/solvent-free/90 °C[27]	10	87
		DABCO/*t*-BuOH/60–65 °C[32]	720	74
		TBABr/*t*-BuOH/80 °C[25]	420	80

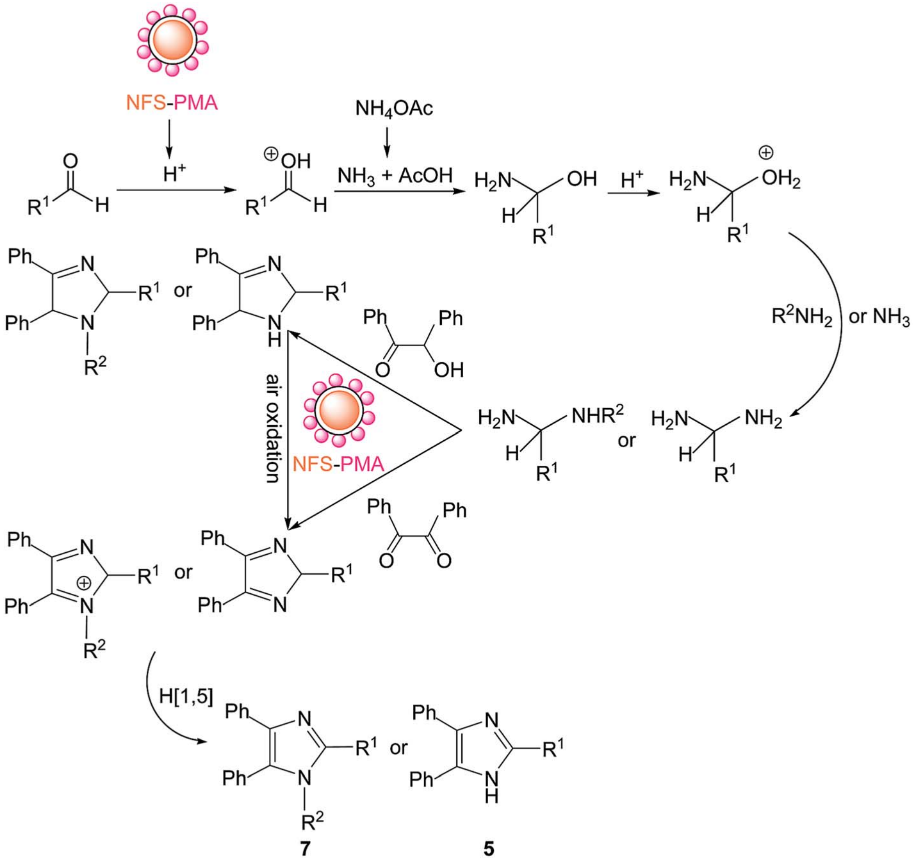
stirred at 120 °C in an oil bath for the times shown in Table 2. Upon completion of the reaction, as indicated by TLC (hexane : ethyl acetate, 8 : 2), hot EtOH (96%, 1 mL) was added to the mixture and stirred for 2 min and, then, the nanomagnetic catalyst was separated from the reaction mixture by employing an external magnetic field. After that, the reaction mixture was poured onto crushed ice and the precipitated solid was collected, and recrystallized from ethanol (96%, 3 mL) to afford the pure 2,4,5-trisubstituted imidazole derivatives (**5a–i**). All products are known compounds, which were characterized by measuring their m.p., and by IR and ^{1}H-NMR spectroscopies.

General procedure for the synthesis of 1,2,4,5-tetrasubstituted imidazoles (7a–j)

A mixture of benzil or benzoin (1 mmol), aldehyde (1 mmol), ammonium acetate (7 mmol), benzylamine (2 mmol) and NFS–PMA (0.02 g) was stirred at 120 °C in an oil bath for the times shown in Table 2. Upon completion of the reaction as indicated by TLC (hexane : ethyl acetate, 8 : 2), hot EtOH (96%, 1 mL) was added to the mixture and stirred for 2 min and, then, the nanomagnetic catalyst was separated from the reaction mixture by employing an external magnetic field. After that, the reaction mixture was poured onto crushed ice and the precipitated solid was collected, and recrystallized from ethanol (96%, 3 mL) to afford the pure 1,2,4,5-tetrasubstituted imidazole derivatives (**7a–j**). All products are known compounds, which were characterized by measuring their m.p., and by IR and ^{1}H-NMR spectroscopies.

Conclusions

In summary, we have demonstrated an efficient and mild procedure for the synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles in the presence of NiFe$_2$O$_4$@SiO$_2$–H$_3$PMo$_{12}$O$_{40}$ as a reusable, eco-friendly, inexpensive and efficient nanocatalyst. Moreover, other advantages such as excellent product yields, very short reaction times, mild reaction conditions, and simple work-up procedures make this method an interesting alternative to other methodologies. In addition, it is easy to separate and recover the catalyst for another catalytic recycling.



Scheme 3 Proposed mechanism.

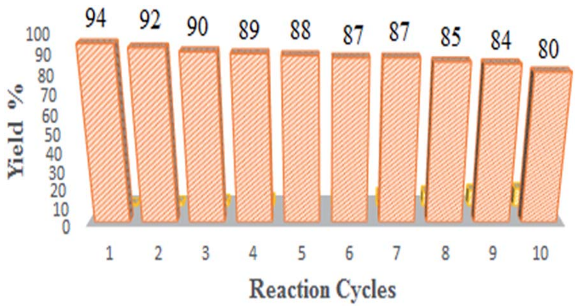


Fig. 5 Reusability of $NiFe_2O_4@SiO_2-H_3PMo_{12}O_{40}$ (NFS–PMA) for the model reaction.

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