Preparation of carboxylic acid functionalized organosilan on ferrite-silica nanoparticles and evaluation of their catalytic activity in synthesis of oxindoles

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Carboxylic acid functionalized organo silan on ferrite-silica nanoparticles were prepared in four steps: (i) preparation of colloidal iron oxide magnetite nanoparticles (Fe_3O_4 MNPs), (ii) coat silica on Fe_3O_4 MNPs (Fe_3O_4@SiO_2 MNPs), (iii) functionalization of organo silan of (3-aminopropyl) trimethoxy silane on ferrite-silica nanoparticles (Fe_3O_4@SiO_2@PA) and (iv) incorporation of carboxylic acid as a functional group on the surface of ferrite-silica-organo silan nanoparticles (Fe_3O_4@SiO_2@PA@COOH). The properties of prepared magnetite nanocomposite were characterized by infrared (FT-IR), vibrating sample magnetometer (VSM), X-ray diffraction analysis (XRD), thermal gravimetric analysis (TGA), Energy-Dispersive X-ray (EDX) and scanning electron microscopy (SEM) spectroscopy. The prepared magnetic catalysts (Fe_3O_4@SiO_2@PA@COOH) showed high catalytic activity for the synthesis of diindolyl oxindoles by the coupling of indole and isatin compounds with good to high yields in aqueous medium.

Keywords: Fe_3O_4@SiO_2@PA@COOH, magnetite nanocomposite, indole, isatin, diindolyloxindoles.

Introduction

Heterogeneous catalysts with a matrix structure generally as the magnetically recyclable catalysts are developed in recent years and can be very useful to assist an effective separation and recovery in a liquid-phase reaction by a magnet, especially when the catalysts are in the nanometer-sized range and possess higher activities than their pure and bulk single-metal or non-metal counterparts[1–3]. Magnetic nanosized particles have already been known for over 50 years, but research into their potential use in medicine and pharmaceutics is now the hot topic in this domain[4,5]. Magnetic nanoparticles in particular might contribute to such applications due to their distinct advantages like high surface area-to-volume ratio and therefore higher extraction capacity compared to micrometer-sized particles. The most important benefits are the facile and convenient separation by applying an external magnetic field enabling an easy recovery and recycling of the scavenger, potentially even in the open environment[6,7]. According to these attractive properties, many MNP supported catalysts have been designed and widely applied as novel magnetically separated catalysts in traditional metal catalysis[8–10], organocatalysis[11] and even enzyme catalysis[12]. Recently, nanocrystalline ferrite is one of the most attractive class of materials that has been intensively investigated as one of the magnetic nanomaterials in various organic reaction.

Spirooxindoles occupy an important place in the area of heterocyclic chemistry because they are frequently found in numerous natural and synthetic products along with useful biopharmaceutical, physiopharmaceutical, and pharmaceutical activities such as antibacterial, antiprotozoal, anti-inflammatory activities and progesterone receptors (PR) agonists. As a consequence, great efforts have been devoted to the construction of diversely structured spirooxindole-fused heterocycles in the past few years[13–15]. Despite the availability of these methods, because of the importance of these heterocyclic compounds from pharmaceutical, industrial, and synthetic points of view, there still remains a high demand for the development of an efficient, general, low-cost, and clean protocol to assemble these compounds.

In this paper, we propose to carboxylic acid functionalized organo silan supported on ferrite-silica nanoparticles (Fe_3O_4@SiO_2@PA@COOH) as nanocatalyst with large den-

sity of acidic groups were synthesized using chemical methods. The present work provided a nanocatalys for potential synthetic application. In the present study shows unique advantages, such as high magnetic property, high density of acid functional groups of the nanoparticle surface, simple synthesis of the catalyst and easy separation of catalyst with a permanent magnet. Also, $Fe_3O_4@SiO_2@PA@COOH$ MNPs are efficient and reusable nanocatalysts for the synthesis of diindolyl oxindole derivatives. Product has been achieved by a one-pot coupling reaction of isatin compounds and indoles in a short period of time.

Experimental

Chemicals: All starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Purity determinations of the products were accomplished by TLC on silica-gel polygram SILG/UV 254 plates. Melting points were measured on an Electro thermal 9100 apparatus. IR spectra were taken on a Perkin-Elmer 781 spectrometer in KBr pellets and reported in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker DPX-250 Avance instrument at 250 MHz and 62.9 MHz in $CDCl_3$ or DMSO-d_6 with chemical shift given in ppm relative to TMS as internal standard. Power X-ray diffraction (XRD) was performed on a Bruker D_8-advance X-ray diffractometer with Cu K_α (λ = 0.154 nm) radiation. The magnetic properties were determined by using vibrating sample magnetometer (VSM) leak shore 7200 at 300 KVsm leak shore.

Catalyst preparation

Preparation of Fe_3O_4 nanoparticles: Firstly, 15 g sodium hydroxide (NaOH) was dissolved into 25 mL deionized water. Then, the mixture of 2 g $FeCl_2.4H_2O$, 5.2 g $FeCl_3.6H_2O$, 25 mL deionized water and 0.85 mL HCl wsa added drop by drop with vigorous stirring to make a black solid product. The resultant mixture was heated on water bath for 4 h at 80°C. The black magnetite solid MNPs were isolated by an external magnet and washed with deionized water and ethanol three times and was then dried at 80°C for 10 h.

Preparation of $Fe_3O_4@SiO_2$ core-shell: Fe_3O_4 (0.50 g, 2.1 mmol) was dispersed in the mixture of ethanol (100 mL) and deionized water (20 mL) for 10 min. Then 2.5 mL of NH_3 was added followed by the addition of tetraethoxysilane (TEOS) (1.5 mL) drop by drop. This solution was stirred

mechanically for 6 h at room temperature. Then the product $Fe_3O_4@SiO_2$ was separated by an external magnet and was washed with deionized water and ethanol three times and dried at 80°C for 10 h.

Preparation of $Fe_3O_4@SiO_2$ bonded propyl amine ($Fe_3O_4@SiO_2@PA$): $Fe_3O_4@SiO_2$ (0.5 g) was dispressed in dry toluene (50 mL) for 1 h and then 3-aminopropyl trimethoxy silane (1.5 mL) was added followed by NaH (0.012 g). The suspension was mechanically stirred as it was heated under reflux for 48 h. $Fe_3O_4@SiO_2$ bonded propyl amine MNPs were isolated by an external magnet. The collected powder was washed using toluene and ethanol and were dried under vacuum at 80°C for 4 h to give $Fe_3O_4@SiO_2@PA$.

Preparation of $Fe_3O_4@SiO_2$ bonded propyl amin-carboxylic acid [$Fe_3O_4@SiO_2@PA@COOH$]: To a magnetically stirred mixture of $Fe_3O_4@SiO_2@PA$ (0.1 g) in $CHCl_3$ (10 ml) at 50°C, maleic anhydride (2 g) was added and stirred for 5 h. $Fe_3O_4@SiO_2@PA@COOH$ MNPs were isolated by an external magnet and were washed with methanol and diethyl ether (30 ml) and then dried at room temperature to give $Fe_3O_4@SiO_2@PA@COOH$.

General procedure for the preparation of diindolyloxindole derivatives: The reactions were carried out by mixing the indole compounds (2 mmol) and isatin compounds (1 mmol) in the presence of $Fe_3O_4@SiO_2@PA@COOH$ MNPs (0.025 g) in aqueous medium that stirred at 80°C in oil bath for 15 min. Thin layer chromatography clearly indicated the formation of corresponding oxindole. After completion of the reaction, the mixture was dissolved in acetone and $Fe_3O_4@SiO_2@PA@COOH$ MNPs were separated by external magnet. Then the solvent was removed from solution under reduced pressure to produce oxindole product. The product was purified by recrystallization using methanol to afford the pure product. The spectroscopic and analytical data for the prepared compounds are presented below.

5-Bromo-1-ethyl-3,3-bis(1-methyl-1H-indol-3-yl) indolin-2-one (entry 3): White solid, m.p. 250°C; ^{1}H NMR (250 MHz, DMSO-d_6): 1.26 (t, 3H, *J* 7.6 Hz, CH_3-CH_2), 3.37 (q, 2H, *J* 7.6 Hz, CH_2-CH_3), 3.8 (s, 6H, CH_3), 6.83–6.91 (m, 4H), 7.06–7.20 (m, 4H), 7.30–7.40 (m, 2H), 7.49–7.54 (m, 4H); ^{13}C NMR (62.9 MHz, DMSO): 12.9 (CH_3), 32.7 (CH_2), 52.7 (C), 110.7 (C-H), 111.8 (C-H), 112.8 (C-H), 114.4 (C), 119.4 (C-H), 121.2 (C-H), 121.9 (C-H), 126.2 (C-H), 128.7 (C-H), 129.3 (C-H), 131.5 (C), 136.7 (C), 137.7 (C-H), 141.7 (C), 176.6 (C=O).

2,2″-Dimethyl-1H,1″H-[3,3′:3′,3″-terindol]-2′(1′H)-one (entry 4): Pinkish solid, m.p. 290°C; ^{1}H NMR: δ 1.93 (s, 3H), 2.07 (s, 3H), 6.45 (d, *J* 7.3 Hz, 1H), 6.58–6.70 (m, 3H), 6.84–6.95 (m, 4H), 7.13–7.23 (m, 4H), 10.51 (s, 1H), 10.83 (s,1H), 10.86 (s, 1H); ^{13}C NMR: δ 179.8, 141.7, 136.1, 135.5, 135.4, 134.4,132.5, 128.3, 128.2, 127.5, 125.9, 121.7, 120.2, 120.0, 119.8, 119.8, 118.4, 118.4, 110.9, 110.8, 109.9, 52.9, 13.6, 13.4.

1H,1″H-[3,3′:3′,3″-terindol]-2′(1′H)-one (entry 5): White solid, m.p. 319°C (dec.); ^{1}H NMR: δ 6.78–7.03 (m, 8H), 7.23 (d, *J* 4.8 Hz, 4H), 7.35 (d, *J* 6.7 Hz, 2H), 10.60 (s, 1H), 10.95 (s, 2H); ^{13}C NMR: δ 179.2, 141.8, 137.4, 135.1, 128.3, 126.2, 125.4, 124.8, 121.9, 121.4, 121.3, 118.7, 114.8, 112.1, 110.0, 53.1.

5-Bromo-1H,1″H-[3,3′:3′,3″-terindol]-2′(1′H)-one (entry 6): White solid, m.p. 302°C (dec.); ^{1}H NMR: δ 6.79–7.04 (m, 6H), 7.13–7.27 (m, 4H), 7.35 (dd, *J* 6.1, 6.1 Hz, 2H), 7.44 (s, 1H), 10.65 (s, 1H), 10.97 (s, 1H), 11.20 (s, 1H); ^{13}C NMR: δ 179.1, 141.8, 137.4, 136.2, 134.6, 128.5, 128.0, 126.3, 126.0, 125.4, 124.8,124.0, 123.7, 122.1, 121.5, 120.7, 118.9, 114.6, 114.5, 114.2, 112.2, 111.4,110.2, 52.8.

7-Methyl-1H,1″H-[3,3′:3′,3″-terindol]-2′(1′H)-one (entry 7): Yellow solid, m.p. 220°C; ^{1}H NMR: δ 2.45 (s, 3H), 6.73 (dd, *J* 7.1, 7.3 Hz, 1H), 6.80–6.87 (m, 4H), 6.94 (dd, *J* 6.8, 7.0 Hz, 1H), 7.00–7.06 (m, 3H), 7.22–7.31 (m, 3H), 7.37 (d, *J* 7.8 Hz, 1H), 10.62 (s, 1H), 10.95 (s, 1H), 10.98 (s, 1H); ^{13}C NMR: δ 179.3, 141.8, 137.4, 136.9, 135.2, 128.3, 126.2, 125.9, 125.4, 124.7, 124.5, 121.9, 121.5, 121.4, 121.0, 119.0, 118.8, 118.7, 115.3, 114.8, 112.1, 110.0, 53.1, 17.2.

5-Bromo-3,3-bis(1-methyl-1H-indol-3-yl) indolin-2-one (entry 10): White solid, m.p. 250°C; ^{1}H NMR (250 MHz, DMSO-*d$_6$*) 3.81 (s, 6H, CH$_3$), 6.80–6.91 (m, 4H), 7.03–7.25 (m, 4H), 7.32–7.45 (m, 2H), 7.50–7.50 (m, H); ^{13}C NMR (62.9 MHz, DMSO): 52.7 (C), 111.7 (C-H), 111.2 (C-H), 112.1 (C-H), 114.7 (C), 119.8 (C-H), 122.0 (C-H), 121.3 (C-H), 126.8 (C-H), 128.4 (C-H), 129.0 (C-H), 131.2 (C), 136.9 (C), 137.1 (C-H), 141.3 (C), 176.0 (C=O).

Results and discussion

In this study, we report the synthesis of a carboxylic acid supported on Fe$_3$O$_4$@SiO$_2$@organosilan magnetic particle with a high density of acidic groups for the first time. This nanocatalyst was prepared in four steps: (i) preparation of colloidal iron oxide magnetic nanoparticles (Fe$_3$O$_4$ MNPs): Fe$_3$O$_4$ MNPs were prepared by the reaction of FeCl$_2$.4H$_2$O, FeCl$_3$.6H$_2$O with sodium hydroxide in deionized water, (ii) coat silica on Fe$_3$O$_4$ MNPs: to mixture Fe$_3$O$_4$ and tetraethoxysilane (TEOS) was added NH$_3$ and was stirred mechanically at room temperature to produce Fe$_3$O$_4$@SiO$_2$ MNPs, (iii) functionalization of organo silan of (3-aminopropyl) trimethoxy silane on ferrite-silica nanoparticles and (Fe$_3$O$_4$@SiO$_2$@PA): Fe$_3$O$_4$@SiO$_2$ MNPs were reacted with (3-aminopropyl) trimethoxy silane in dry toluene under reflux for 48 h and (iv) incorporation of carboxylic acid as a functional group on the surface of ferrite-silica nanoparticles (Fe$_3$O$_4$@SiO$_2$@PA@COOH): Fe$_3$O$_4$@SiO$_2$@PA MNPs were treated with maleic anhydride in chloroform for 5 h to give (Fe$_3$O$_4$@SiO$_2$@PA@COOH MNPs) (Scheme 1).
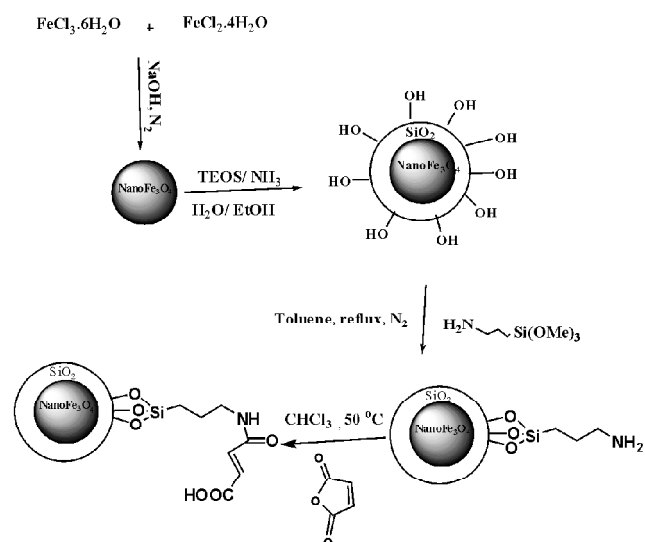
Scheme 1. Preparation of Fe$_3$O$_4$@SiO$_2$@PA@COOH MNPs.

Characterization of Fe$_3$O$_4$@SiO$_2$@PA@COOH MNPs

The synthesized catalyst was characterized by different methods such as SEM, IR, VSM, XRD.

EDX and SEM analyses: Figs. 1–3 shows energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$ and Fe$_3$O$_4$@SiO$_2$@PA@COOH MNPs. The results demonstrate that Fe and Fe, Si appear in Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$ MNPs samples. Also, they demonstrate that Si, Fe, O, C and N appear in Fe$_3$O$_4$@SiO$_2$@PA@COOH MNPs sample.
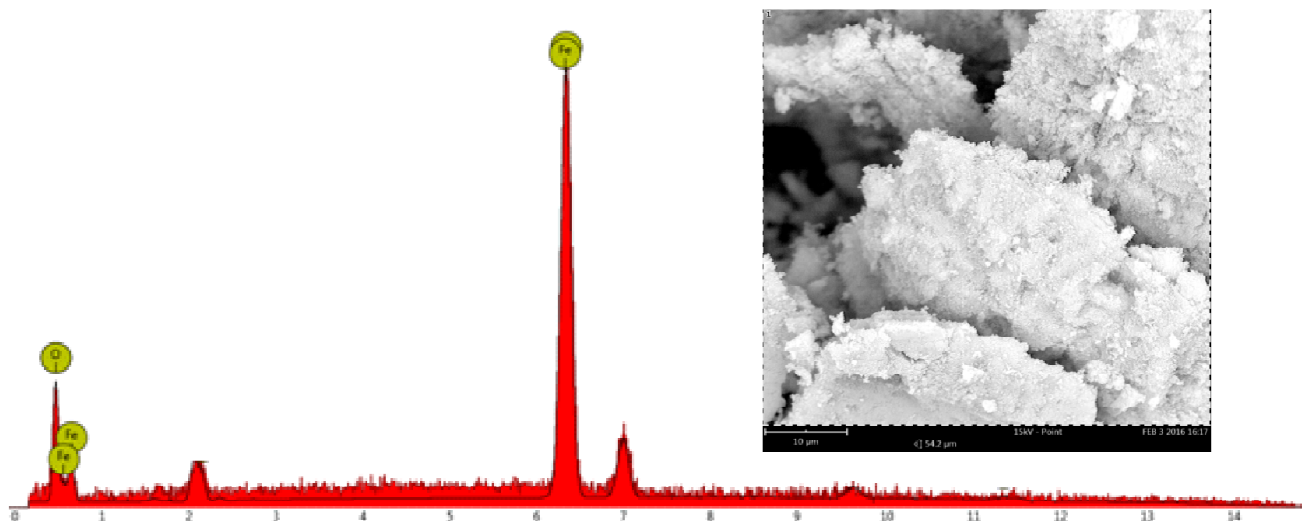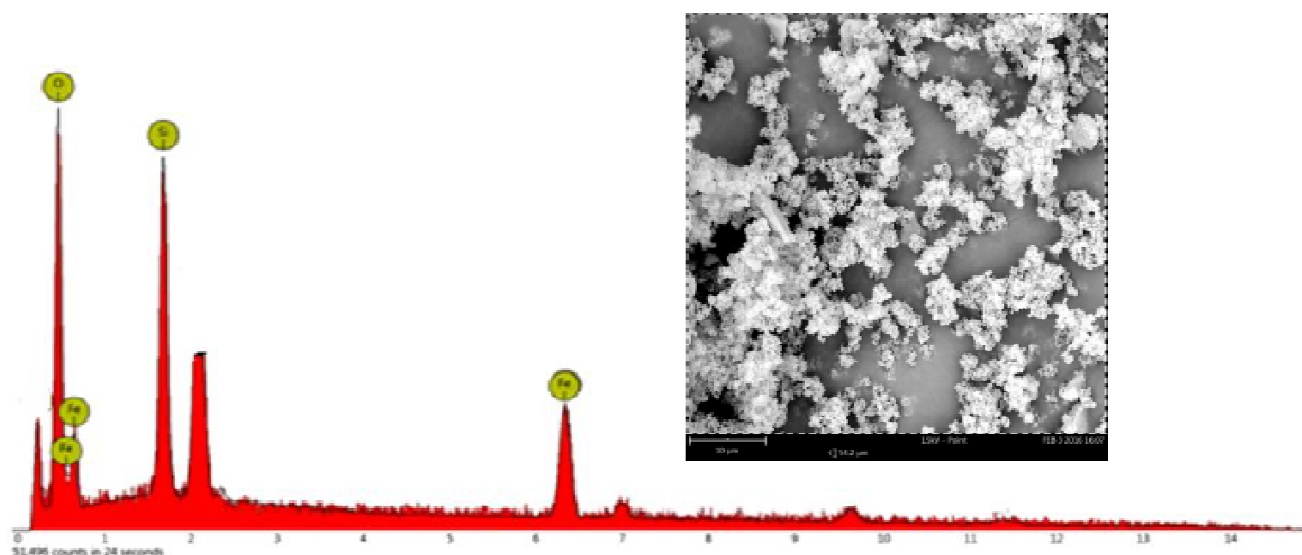
Fig. 1. EDX and SEM pattern of Fe$_3$O$_4$ MNPs.

Fig. 2. EDX and SEM pattern of Fe$_3$O$_4$@SiO$_2$ MNPs.

XRD study: The powder X-ray pattern recorded for the sample of Fe$_3$O$_4$@SiO$_2$@PA@COOH MNPs are shown in Fig. 4. XRD patterns of the synthesized Fe$_3$O$_4$@SiO$_2$@PA@COOH nanoparticle display several relatively strong reflection peaks in region of 20–80°C, at 2θ: 30.2, 35.3, 43.2, 53.5, 57 and 62.5, which are assigned to the (220), (311), (400), (422), (511) and (440) crystallographic faces of magnetite. An obvious diffusion peak at 13–28 was showed that appeared because of the existence of amorphous silica. The calculated average crystallite size, *D* is 8.6–10.2 nm. Using Scherrer's equation $D = 0.9\lambda/\beta \cos\theta$ where *D* is the crystallite size, *k* = 0.9 is a correction factor to account for particle shapes, β is the full width at half maximum (FWHM) of the peaks of all planes in the XRD pattern, λ is the wavelength of Cu target = 1.5406 Å and θ is the Bragg angle. According to the result calculated by Scherrer equation, it was found that the diameter of Fe$_3$O$_4$@SiO$_2$@PA@COOH nanoparticles were obtained 12–14 nm.
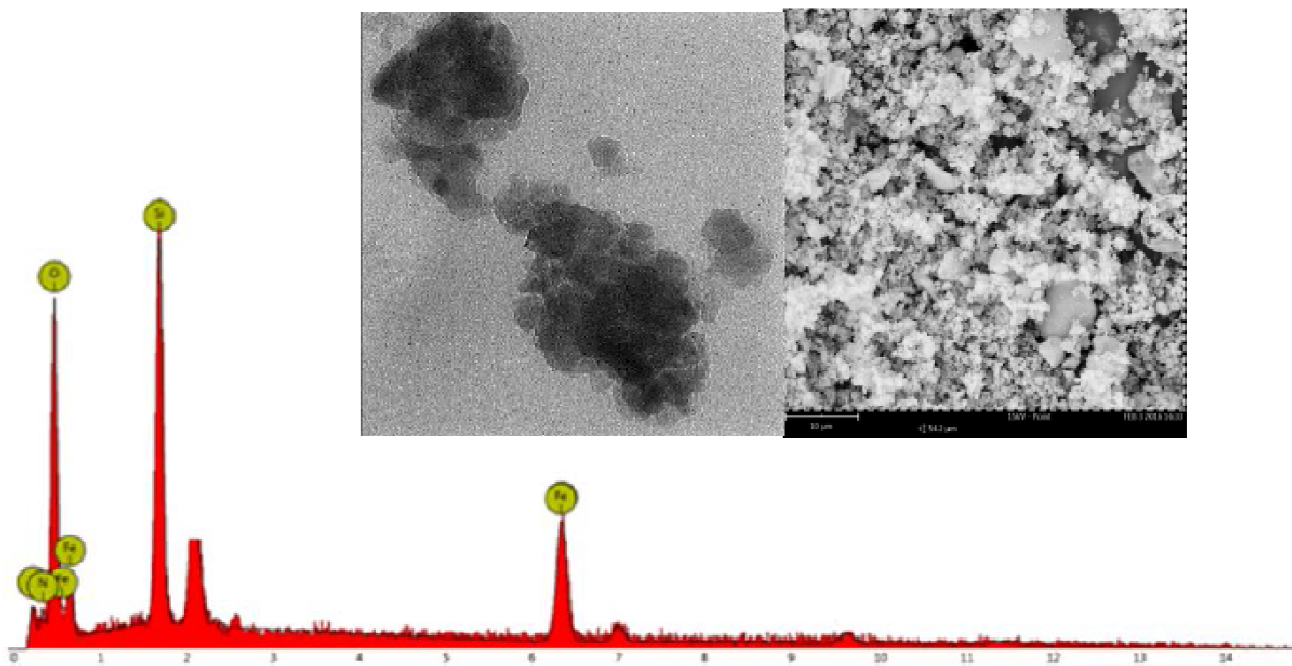
VSM study: Using a VSM at room temperature (300 K),

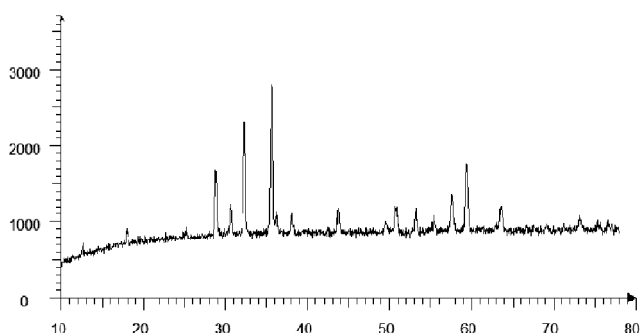**Fig. 3.** EDX and SEM pattern of Fe_3O_4@SiO_2 @PA@COOH MNPs.

Fig. 4. XRD pattern of Fe_3O_4@SiO_2@PA@COOH MNPs.

the hysteretic curve of the Fe_3O_4@SiO_2@PA@COOH nanoparticles is investigated. Plots of magnetization versus magnetic field for Fe_3O_4@SiO_2@PA@COOH nanoparticles are illustrated in Fig. 5. Fe_3O_4@SiO_2@PA@COOH nanoparticles exhibit superparamagnetic behaviour with the saturation magnetisation (Ms) of 32.3 emu g^{-1} and without magnetic hysteresis area, coercivity (Hc) and remanent magnetisation (Mr). This is a characteristic of superparamagnetism.

FT-IR study: The successful conjugation of carboxylic acid onto the surface of the ferrite-silica-organometal sample is further suppor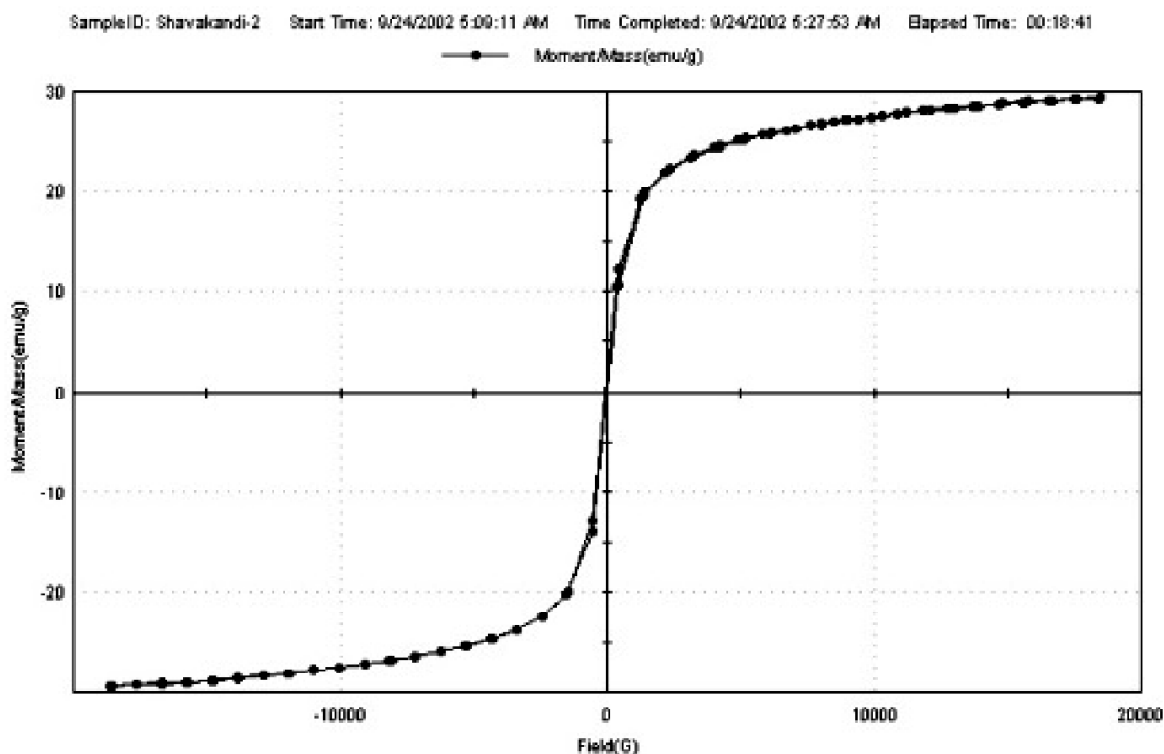ted by FT-IR spectrum shown in Fig. S1 (Supplementary). The bands at 1120 cm^{-1} and 690 cm^{-1} are correspondingto the Si-O and Fe-O groups, respectively. The peaks at 1620 and 1750 are ascribed to carbonyl groups of amide and acid.

Application of Fe_3O_4@SiO_2@PA@COOH MNPs

In order to show the merit of synthesized nanocatalyst in organic reactions, Fe_3O_4@SiO_2@PA@COOH MNPs were used for the synthesis of oxindoles. Initially, the efficacy of various catalysts was examined for the model reaction of isatin and indole. The results are summarized in Fig. 6. Various nanocatalysts including Al_2O_3, Fe_3O_4, SiO_2, Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2@PA@COOH were screened in our model reaction. Among them, Fe_3O_4@SiO_2@PA@COOH MNPs were proven to be the most efficient catalyst for this reaction (75%). It was showed that the reaction was rather sluggish and resulted in poor yield (17%) in the absence of catalysts when the reaction was carried out in water for 15 min at 80°C, which indicated that the catalysts should be necessary for this transformation.

Optimization of the reaction conditions

The preceding reaction was also examined in various solvents (Fig. 7). The results indicated that a very low yield of the desired product was obtained when dichloromethane,

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SampleID: Shavakandi-2   Start Time: 9/24/2002 5:09:11 AM   Time Completed: 9/24/2002 6:27:53 AM   Elapsed Time: 00:18:41

Coercivity (Hci): 14.667 G   Initial Slope: 9.8054E-3 emu/(g G   Magnetization (Ms): 29.408 emu/g
Mass: 14.340E-3 g   Negative Mci: -39.038 G   Negative Mr: 0.25066 emu/g
Negative Ms: -29.408 emu/g   Positive Mci: -9.7029 G   Positive Mr: 1.0295 emu/g
Positive Ms: 29.408 emu/g   Retentivity (Mr): 0.38941 emu/g

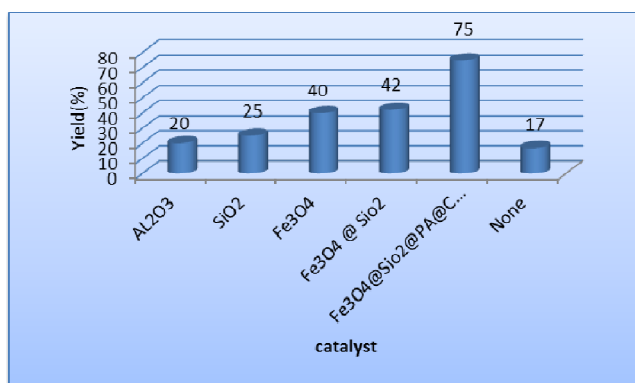**Fig. 5.** VSM pattern of Fe_3O_4@SiO_2@PA@COOH MNPs.

Fig. 6. One-pot synthesis of diindolyl oxindole in the presence of various catalytic systems.
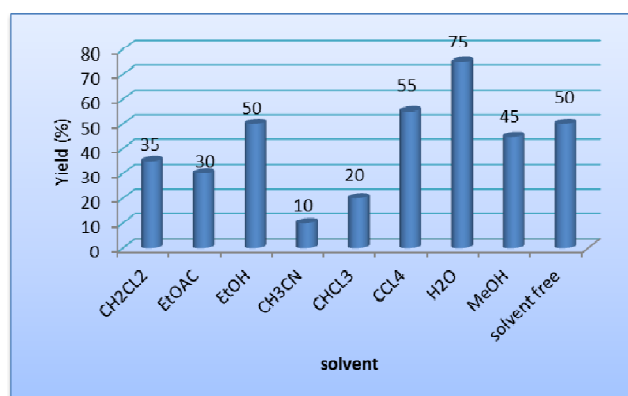

Fig. 7. Effect of solvent on the synthesis of diindolyl oxindole by Fe_3O_4@SiO_2@PA@COOH MNPs.

acetonitrile, ethyl acetate were used as solvents. The best yield was obtained when the reaction was performed in water, which may be attributable to the proton nature of water, and it accelerated the reaction compared with other solvents and solvent-free condition.

We also examined the influence of temperature on the reaction yields. It was found that no desired product was obtained at room temperature. The reaction yield dramatically increased from 0% to 90% when the reaction temperature increased from 25°C to 100°C. As Fig. 8 indicates, the
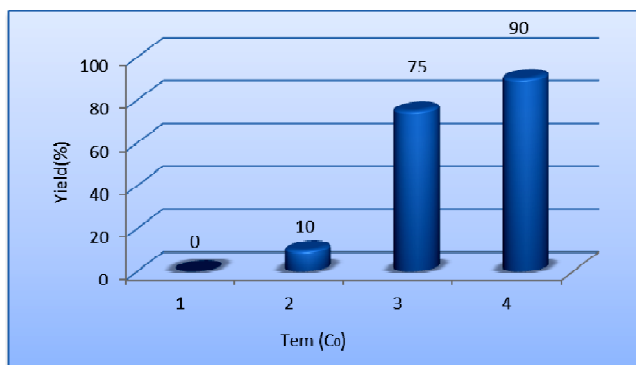
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Fig. 8. Effect of temperature on the synthesis of diindolyl oxindole.

reasonable results were observed when the reaction was performed at 80°C. Increment of the temperature up to 80°C didn't significantly improve the reaction results.

In another study, this reaction was tested in the presence of different molar ratios of $Fe_3O_4@SiO_2@PA@COOH$ MNPs at 80°C in aqueous medium (Fig. 9). It was observed that the use of 0.003 g nanocatalyst is sufficient to promote the reaction. Larger amount of the nanocatalyst did not improve the
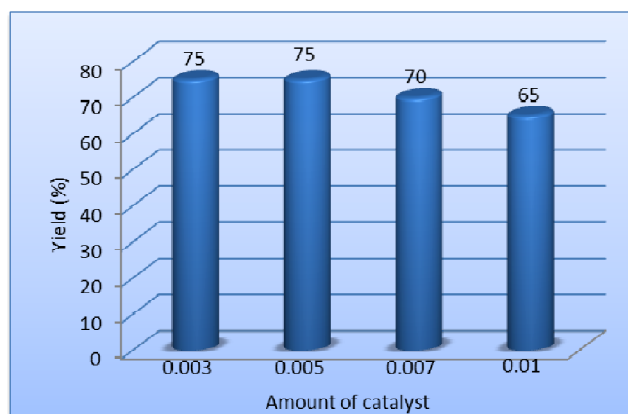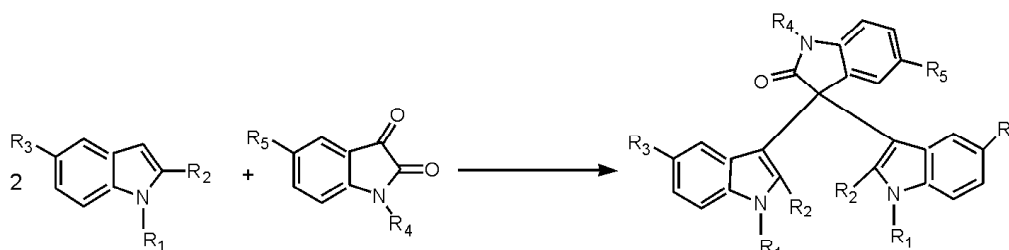

Fig. 9. Effect of the amount of nanocatalyst on the synthesis of diindolyl oxindole.

yields. Decreasing the catalyst concentration resulted in lower yields under the same conditions.

Extension of substrate scope

In order to establish the generality of this method, the synthesis of various diindolyl oxindoles was studied using

Table 1. Preparation of 3,3-diindolyloxindoles by $Fe_3O_4@SiO_2@PA@COOH$ MNPs[a]

Entry	Reagent					Time	Yield
	Indol			Isatin		(min)	(%)
	R_1	R_2	R_3	R_4	R_5		
1	H	Me	H	H	Br	30	90
2	H	Me	H	H	Me	30	80
3	Me	H	H	CH_2CH_3	Br	30	75
4	H	Me	H	H	H	30	80
5	H	H	H	H	H	30	75
6	H	H	H	H	Br	30	85
7	H	H	H	H	Me	90	65
8	Me	Me	H	H	H	30	75
9	Me	H	H	H	H	25	75
10	Me	H	H	H	Br	35	60

[a]Reaction conditions: isatin compounds (1 mmol), indole compounds (2 mmol), $Fe_3O_4@SiO_2@PA@COOH$ MNPs (0.003 g) and water (2 mL) at 80°C. [b]The yield refers to pure isolated product.

different indoles and isatins under optimized reaction conditions (0.003 g of Fe_3O_4@SiO_2@PA@COOH MNPs in aqueous medium at 80°C). The results are summarized in Table 1. As the results of Table 1 indicate, diindolyl oxindoles were produced from the reaction of various substituted isatin and indole in good to high yields (75–90%). 5-Bromo isatin as more reactive carbon electrophile underwent the condensation reaction to afford the corresponding oxindole in good yields (Table 1, entries 1, 6). Also, the reaction time of indole and isatin compounds was longer than those of 2-methylindole. This behavior could result from the more reactivity of 2-methylindole due to methyl group.

At the end of the reaction, the catalyst could be recovered by external magnetic field. The recycled catalyst was washed with dichloromethane and subjected to a second reaction process. The results show that the yield of product after four runs was only slightly reduced (Fig. 10).
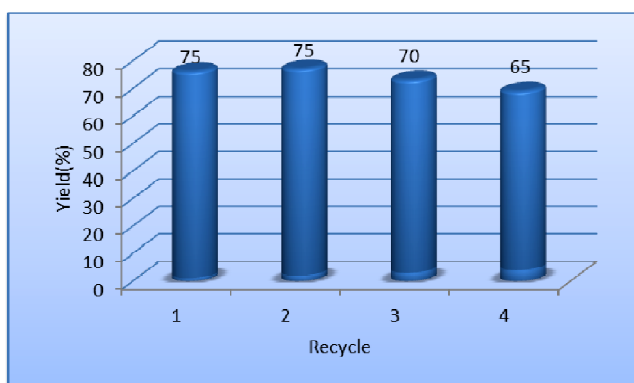

Fig. 10. Recyclability of Fe_3O_4@SiO_2@PA@COOH MNPs in the synthesis of diindolyl oxindole.

Conclusions

In summary, in this paper, carboxylic acid functionalized organo silan supported on ferrite-silica nanoparticles (Fe_3O_4@SiO_2@PA@COOH) were successfully synthesized as new acidic nano catalyst. It was applied as a magnetically recyclable heterogeneous catalyst for the one-pot, psoudo three-component synthesis of diindolyl oxindole. This catalyst efficiently promoted the condensation of indol and isatin in good to high yields aqueous medium. Product separation and catalyst recycling are easy and simple with the assistance of an external magnet. The catalyst can be recovered and reused for five times without significant degradation in activity.

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