

# Synthesis of amidoalkyl naphthols via $\text{AlCl}_3$ functionalized silica-coated $\text{Fe}_2\text{O}_3$ magnetic nanoparticles as a new, efficient, and eco-friendly catalyst

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**Abstract** Nano  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  is synthesized and applied as a recyclable catalyst for cost-effective synthesis of amidoalkyl naphthols, from aldehydes, 2-naphthols, and amides (or urea). This heterogeneous catalyst enhances product purity and can efficiently be removed by an external magnet. Characterization of the catalyst is carried out by SEM, XRD, ICP, TGA, and VSM. The thermal solvent-free procedure offers advantages such as shorter reaction times, simple work-ups, excellent yields, and reusability of the catalyst.

**Keywords** Nano · Amidoalkyl naphthols · Recyclable catalyst · Maghemite · Green chemistry

## Introduction

Multicomponent reactions (MCRs) are special types of synthetically useful processes in which three or more different starting materials react to give a final product in a one-pot procedure [1–5]. MCRs have drawn a great deal of attention for increasing the efficiency by combining several operational steps without any need for isolation of intermediates or changing the reaction conditions. MCRs are becoming powerful tools in modern synthetic chemistry due to their efficiency, atom economy, and convenience in the construction of multiple new bonds in one-pot processes. They play powerful roles in approaching complex structures and promote ‘green chemistry’ [6–8].

For instance, amidoalkyl-2-naphthol derivatives can be easily converted to important biologically active compounds such as aminoalkyl-2-naphthols by an amide hydrolysis reaction. Several Lewis and Brønsted acids have been applied for this transformation including  $\text{Ce}(\text{SO}_4)_2$  [9], Montmorillonite K10 [10], iodine [11], cation-exchanged resins [12],  $\text{NaHSO}_4\cdot\text{H}_2\text{O}$  [13],  $\text{Fe}(\text{HSO}_4)_3$  [14], sulfamic acid/ultrasound [15],  $\text{HClO}_4/\text{SiO}_2$  [16], cyanuric chloride [17], and  $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$  [18]. However, many of the reported methods suffer from one or more of the following drawbacks: (1) low product yield, (2) prolonged reaction time, (3) the use of large amount of reagent, (4) the use of toxic reagents, and (5) incompatibility with the green chemistry. Therefore, search for finding a protocol for the synthesis of aminoalkyl-2-naphthols that are not associated with the above disadvantages is still relevant.

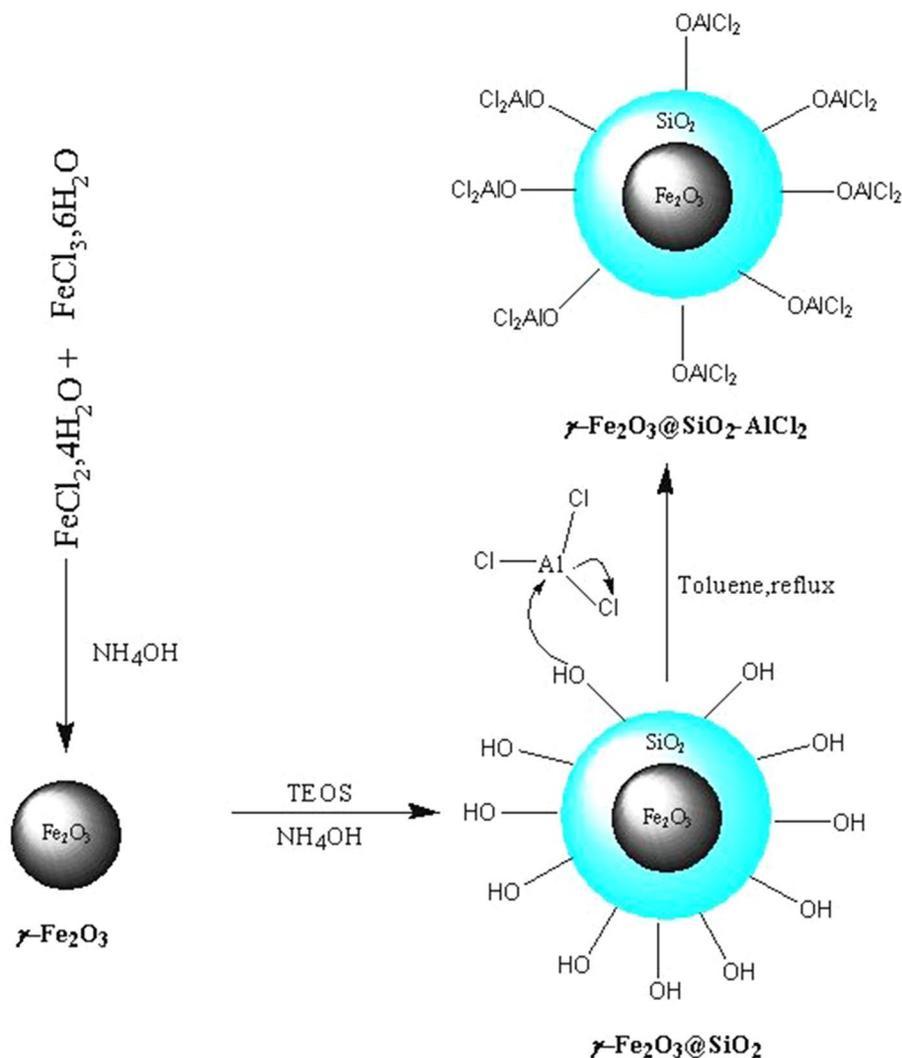
Following our work on “green chemistry” [19–21], we describe an environmentally benign solvent-free approach for the synthesis of amidoalkyl naphthols from aldehydes, 2-naphthols, and amides (or urea), using aluminum chloride functionalized silica-coated  $\text{Fe}_2\text{O}_3$  magnetic nanoparticles, under solvent-free conditions.

## Experimental

Samples are characterized by X-ray diffraction (XRD, Philips Xpert MPD,  $\text{Cu K}\alpha$  irradiation,  $\lambda = 1.54056 \text{ \AA}$ ), scanning electron microscope (SEM, VEGA, TESCAN microscope with an accelerating voltage of 20 kV), energy dispersive X-ray (EDX, INCA, Oxford Instrument). Also,  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  were characterized by thermo-gravimetric analysis (TGA, PerkinElmer) from 25 °C to 900 °C with heating rate of 5 °C under air, ICP, and VSM.

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**Scheme 1** Preparation of  $\text{AlCl}_3$ -functionalized magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles: **a** Fabrication of  $\gamma\text{-Fe}_2\text{O}_3$ , **b** Core-shell formation between  $\gamma\text{-Fe}_2\text{O}_3$  and tetraethyl orthosilicate (TEOS), **c** Functionalization of  $\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2$  with  $\text{AlCl}_3$  and formation of the  $\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2\text{-AlCl}_2$



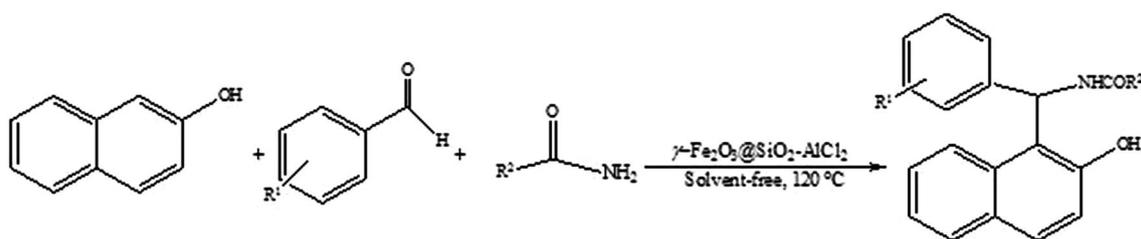
#### Synthesis of aluminum chloride functionalized silica-coated $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles

1.99 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 3.25 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  are separately dissolved in 20 ml water. Mixing is carried out by vigorous stirring (800 rpm). After addition of 0.6 M, 200 mL of  $\text{NH}_4\text{OH}$ , a black precipitate forms at room temperature. To maintain the reaction pH between 11 and 12, a concentrated (25 %, w/w) solution of  $\text{NH}_4\text{OH}$  (30 mL) is added. The black dispersion is continuously stirred for 1 h at ambient. Heating and refluxing it for 1 h yields brown dispersion of  $\gamma\text{-Fe}_2\text{O}_3$ Nps, which is purified through 3 cycles of repeated centrifugation (3000–6000 rpm, 20 min), decantation, and redispersion, until a stable brown magnetic dispersion is obtained (pH 9.4).

$\gamma\text{-Fe}_2\text{O}_3$ Nps (8.5 %, w/w, 20 mL) is dispersed in methanol (80 mL) for 1 h at 40 °C. To it, a concentrated solution

of  $\text{NH}_4\text{OH}$  ammonia is added, and the resulting mixture is stirred for 30 min, at 40 °C. Subsequently, tetraethyl orthosilicate (TEOS, 1.0 mL) is charged to the reaction vessel, and the mixture is continuously stirred for 24 h. The silica-coated nanoparticles ( $\text{SiO}_2@ \text{Fe}_2\text{O}_3$ ) are collected by a permanent magnet, followed by washing three times with EtOH, diethyl ether and drying in vacuum for 24 h, at 100 °C.

10 g of  $\text{SiO}_2@ \text{Fe}_2\text{O}_3$  is dried for 24 h at 120 °C. It is added to a mixture of aluminum trichloride (2.25 g) in 70 mL sodium-dried toluene and stirred at reflux for 2 h. The solvent is removed under vacuum at room temperature (Scheme 1). According to the past TGA reports [30, 31],  $\text{SiO}_2@ \text{Fe}_2\text{O}_3$  nanoparticles is stable under reflux condition for loading  $\text{AlCl}_3$ . Therefore we can do this treatment without any problem and get  $\gamma\text{-Fe}_2\text{O}_3@ \text{SiO}_2\text{-AlCl}_2$  as a nanocatalyst powder.



**Scheme 2** Synthesis of amidoalkyl naphthol over  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$

**Table 1** One-pot synthesis of amidoalkyl naphthols by reaction of aldehydes, amides, and 2-naphthol in presence of the  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$

Entry <sup>a</sup>	R <sup>1</sup>	R <sup>2</sup>	Product	Time (min)	Yield <sup>b</sup> (%)	mp (°C)	mp (lit)	References
1	H	Ph	<b>2a</b>	5	92	240	239–241	[23]
2	3-Nitro	Ph	<b>2b</b>	13	96	240	242–243	[23]
3	4-Methyl	Ph	<b>2c</b>	5	81	214	214–216	[23]
4	4-Methyl	CH <sub>3</sub>	<b>2d</b>	20	82	216	222–223	[25]
5	4-Hydroxy	CH <sub>3</sub>	<b>2e</b>	30	78	208	205–207	[26]
6	3-Nitro	CH <sub>3</sub>	<b>2f</b>	8	96	239	238–240	[24]
7	H	CH <sub>3</sub>	<b>2g</b>	10	89	240	238–240	[24]
8	4-Nitro	CH <sub>3</sub>	<b>2h</b>	7	95	237	237–238	[23]

<sup>a</sup> Reaction conditions: aldehyde (1 mmol), 2-naphthol (1 mmol), amide (1.2 mmol), catalyst (10 mg), 120 °C

<sup>b</sup> Isolated yield

#### General procedure for synthesis of amidoalkyl naphthol over $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$

To a mixture of aldehyde (1 mmol), 2-naphthol (1 mmol), and amide/urea (1.2 mmol) is added,  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  (10 mg) (Scheme 2; Table 1). The mixture is stirred magnetically at 120 °C while the reaction progress is monitored by thin layer chromatography (TLC). After precipitation of the resulting amidoalkyl naphthol, the reaction mixture is cooled to room temperature, and the product is washed with acetone. The catalyst is separated with the aid of an external magnet, and the residue is recrystallized from ethanol.

#### Result and discussion

Here we present data pertaining to a new, efficient, and eco-friendly catalyst ( $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$ ) for synthesis of amidoalkyl naphthols. The results include characterization of the catalyst by SEM, XRD, ICP, TGA and VSM. Then we discuss application of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  as a recyclable catalyst for synthesis of amidoalkyl naphthols, from aldehydes, 2-naphthols and amides (or urea).

#### Synthesis of aluminum chloride functionalized silica-coated $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles

A brown maghemite nanoparticle ( $\gamma\text{-Fe}_2\text{O}_3\text{Nps}$ ) is synthesized by co-precipitation of ferric and ferrous ions in an

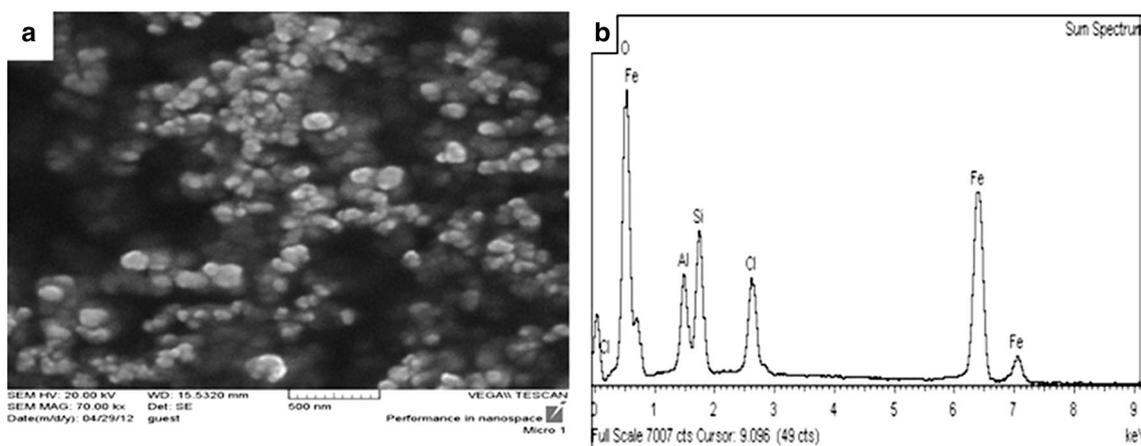
alkali solution. In so doing,  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  are dissolved in water separately and then mixed under vigorous stirring. After addition of  $\text{NH}_4\text{OH}$ , a black precipitate forms at room temperature. To maintain the reaction pH between 11 and 12, a concentrated solution of  $\text{NH}_4\text{OH}$  is added. The black dispersion is continuously stirred at ambient. Heating and refluxing it yields brown dispersion of  $\gamma\text{-Fe}_2\text{O}_3\text{Nps}$ , which is purified through three cycles of repeated centrifugation, decantation, and redispersion, until a stable brown magnetic dispersion is obtained at pH 9.4.

In order to coat  $\gamma\text{-Fe}_2\text{O}_3\text{Nps}$  with a layer of silica, the above colloidal  $\gamma\text{-Fe}_2\text{O}_3\text{Nps}$  is dispersed in methanol and a concentrated solution of  $\text{NH}_4\text{OH}$  ammonia is added. Subsequently, tetraethyl orthosilicate (TEOS) is charged to the reaction vessel, and the mixture is continuously stirred. The silica-coated nanoparticle ( $\text{SiO}_2\text{@Fe}_2\text{O}_3$ ) is collected by a permanent magnet, followed by washing with EtOH, diethyl ether and drying in vacuum.

Adding dried  $\text{SiO}_2\text{@Fe}_2\text{O}_3$  to a mixture of aluminum trichloride in sodium-dried toluene and stirring at reflux gives  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  as a flowable powder (Scheme 1).

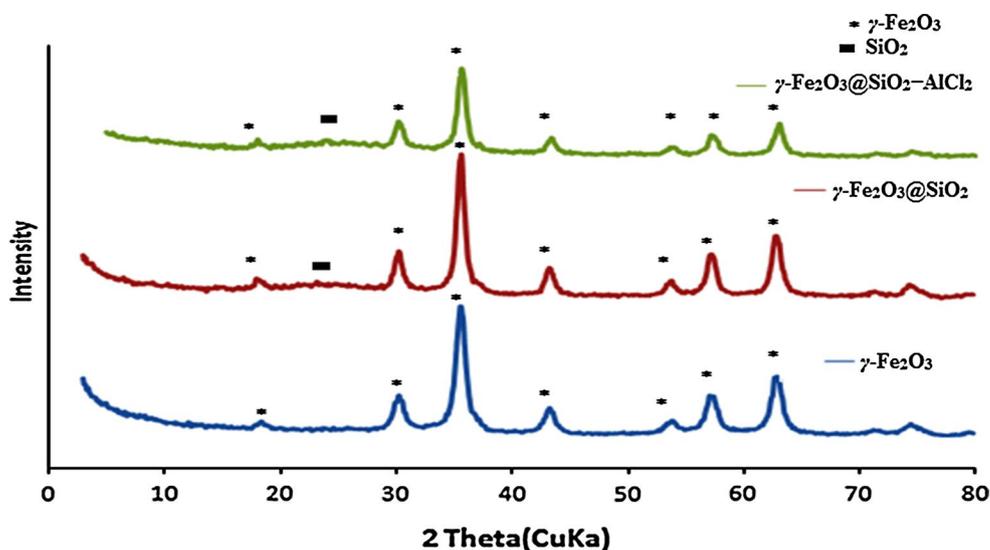
#### Characterization of aluminum chloride functionalized silica-coated $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles

The fair dispersity and spherical morphology of nanocatalyst  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  is indicated by its SEM image (Fig. 1). The nanocatalyst  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  is further



**Fig. 1** The SEM image of the synthesized  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  (a), and its EDX analysis (b)

**Fig. 2** XRD patterns of  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$  and  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$



characterized by EDX analysis which shows peaks corresponding to Fe, Si, Cl, O, and Al elements with weight percentages of 37.4, 8.97, 6.29, 41.4, and 5.94 %, respectively.

The X-ray diffraction patterns of  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$ , and  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  are consistent with their structures (Fig. 2). Specifically, the position and relative intensities of all peaks confirm well with standard XRD pattern of  $\gamma\text{-Fe}_2\text{O}_3$  (JCPDS card No.39-1346) indicating retention of the crystalline cubic structure during functionalization of  $\gamma\text{-Fe}_2\text{O}_3$ . A weak broad band ( $2\theta = 18\text{--}27^\circ$ ) appears in  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$  and  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  which may be assigned to the amorphous silane shell formed around the magnetic cores.

Magnetic properties of  $\gamma\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  NPs are measured by applying an external magnetic field at room temperature. The saturation magnetization values of  $\gamma\text{-Fe}_2\text{O}_3$  NPs and  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  NPs

appear at 60 and 27  $\text{emu g}^{-1}$ , respectively (Fig. 3). Hence, the functionalized magnetic NPs drop upon saturation magnetization. This might be due to the effect of amorphous silica layer coated on the  $\gamma\text{-Fe}_2\text{O}_3$ . In addition, a minimized value of coercivity and negligible magnetization hysteresis found for each sample exhibits superparamagnetic behavior at room temperature. This indicates that the functionalized magnetic NPs are without aggregation.

Thermal stability of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  is probed by TG-DTA in air (Fig. 4). There are three distinct weight loss stages in the TGA curve of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  sample. The first weight loss which ranges from 44 to 242  $^\circ\text{C}$  may be attributed to the evaporation of residual solvents, mainly to the evaporation of the absorbed water. At the second stage, the weight loss from 250 to 548  $^\circ\text{C}$  region can be attributed to the combustion/decomposition of TEOS or APTES molecules. The third stage which appears between 550 and 700  $^\circ\text{C}$

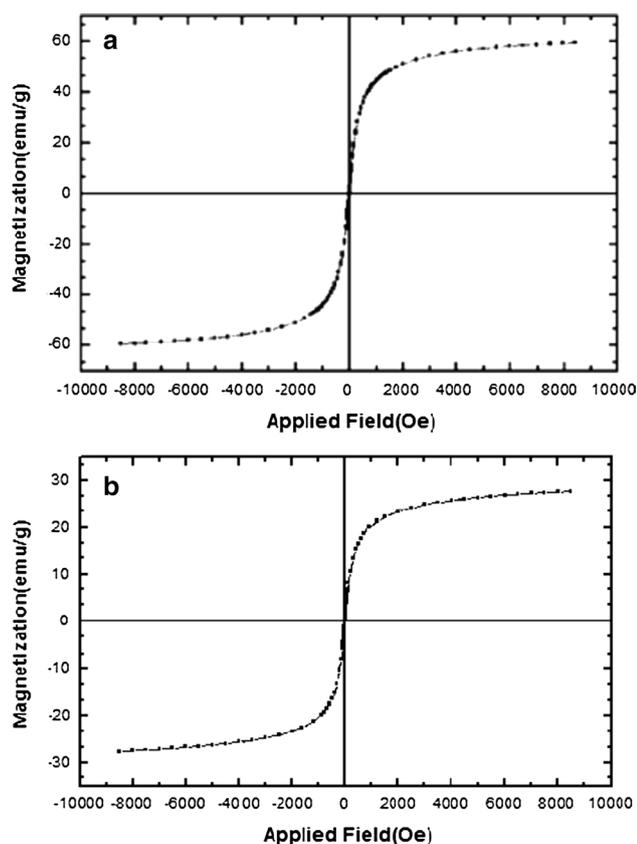


Fig. 3 VSM patterns of  $\gamma\text{-Fe}_2\text{O}_3$  (a), and  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  (b)

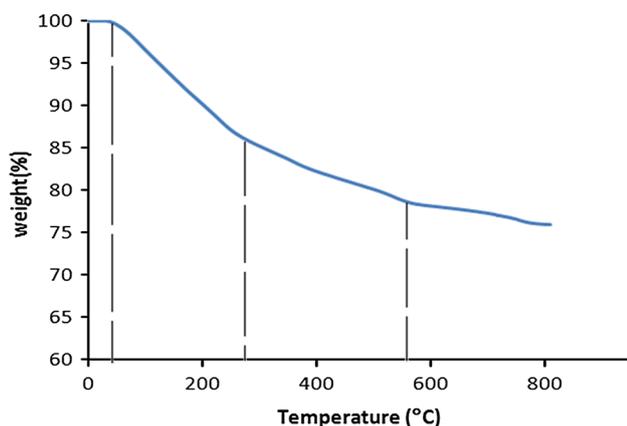


Fig. 4 TGA plot of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$

is associated with the condensation of silanols in the silica shell or the loss of the remaining  $\text{H}_2\text{O}$  molecules embedded within the crystal structure [22]. There is little loss of weight in the TGA curves above 700 °C, showing that the  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  are stable in this temperature range.

ICP detection is developed to determine the percent by weight of the active catalytic species and the amount of

**Table 2** Optimization of the  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  catalyzed model reaction for synthesis of amidoalkyl naphthols

Entry <sup>a</sup>	Catalyst (mg)	Time (min)	Yield <sup>b</sup> (%)
1	No catalyst	60	–
2	2	10	57
3	5	10	65
4	10	10	89
5	20	9	89
6	$\text{AlCl}_3$ (0.5 mol %)	20	53

<sup>a</sup> Benzaldehyde (1 mmol), acetamide (1.2 mmol), 2-naphthol (1 mmol), catalyst, 120 °C

<sup>b</sup> Isolated yield

catalyst loading on  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$ . Results indicate that percent by weight of the active catalytic species and the amount of catalyst loading are 5.47 and 0.02, respectively.

Evaluation of the catalytic activity of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  through synthesis of amidoalkyl naphthols

Catalytic activity of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  is investigated as a heterogeneous catalyst in one-pot synthesis of amidoalkyl naphthols through three-component reaction of aldehydes, amides, and 2-naphthol (Scheme 2). For this purpose, the reaction of benzaldehyde, acetamide, and 2-naphthol as a simple model reaction is probed to establish the feasibility of the strategy and optimize the reaction conditions. Various catalysts are evaluated for this model reaction (Table 2).

The reaction can tolerate a range of aromatic aldehydes carrying either electron-donating or electron-withdrawing substituents in the Meta and Para positions. Electron-withdrawing aldehydes, such as 3-nitro benzaldehyde work well without formation of any side product and give the amidoalkyl naphthol derivative in 96 % yield (Table 1, entry 2). In contrast, aliphatic aldehydes don't expedite the reaction and their yields are very low. Aliphatic amides such as acetamide as well as aromatic amides give good yields of the product (Table 1). All products are characterized on the basis of their spectroscopic data such as FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of products

*N*-((2-hydroxynaphthalen-1-yl) (phenyl) methyl) benzamide (2a)

$^1\text{H}$ NMR (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  = 10.30 (s, 1H), 9.00 (d,  $J$  = 8.6, 1H), 7.84 (m, 3H), 7.78 (d,  $J$  = 8.75, 1H), 7.54 (m, 1H), 7.46 (m, 3H), 7.27 (m, 8H).

$^{13}\text{C}$ NMR (125 MHz, DMSO- $d_6$ ):  $\delta = 165.66, 153.10, 141.93, 134.27, 132.24, 131.35, 129.29, 128.54, 128.43, 128.31, 128.11, 127.05, 126.68, 126.46, 126.36, 122.60, 118.61, 118.27.$

*N*-((2-hydroxynaphthalen-1-yl) (3-nitrophenyl) methyl) benzamide (**2b**)

$^1\text{H}$ NMR (500 MHz, DMSO- $d_6$ ):  $\delta = 10.40$  (s, 1H), 9.12 (s, 1H), 8.09 (s, 3H), 7.85 (d,  $J = 8.7$ , 4H), 7.70 (s, 1H), 7.51 (m, 3H), 7.31 (m, 3H).

$^{13}\text{C}$ NMR (125 MHz, DMSO- $d_6$ ):  $\delta = 166.17, 153.37, 147.74, 144.48, 133.95, 133.23, 132.14, 131.49, 129.92, 129.69, 128.67, 128.38, 128.33, 127.30, 126.97, 122.75, 122.45, 121.57, 120.89, 118.55, 117.22, 48.89.$

*N*-((2-hydroxynaphthalen-1-yl) (*p*-tolyl) methyl) benzamide (**2c**)

$^1\text{H}$ NMR (500 MHz, DMSO- $d_6$ ):  $\delta = 10.27$  (s, 1H), 8.96 (s, 1H), 8.04 (s, 1H), 7.80 (m, 4H), 7.49 (m, 4H), 7.26 (m, 3H), 7.10 (m, 4H), 2.22 (s, 3H).

$^{13}\text{C}$ NMR (125 MHz, DMSO- $d_6$ ):  $\delta = 165.55, 153.03, 138.94, 135.54, 134.34, 132.22, 131.31, 129.19, 128.66, 128.51, 128.44, 128.31, 126.99, 126.63, 126.33, 122.58, 118.64, 118.40, 49.01, 20.47.$

*N*-((2-hydroxynaphthalen-1-yl) (*p*-tolyl) methyl) acetamide (**2d**)

$^1\text{H}$ NMR (500 MHz, DMSO- $d_6$ ):  $\delta = 9.94$  (s, 1H), 8.39 (d,  $J = 8.25$ , 1H), 7.78 (d,  $J = 8$ , 1H), 7.74 (d,  $J = 8.85$ , 1H), 7.33 (m, 1H), 7.24 (m, 1H), 7.19 (d,  $J = 8.8$ , 1H), 7.06 (d,  $J = 8.25$ , 1H), 7.03 (m, 4H), 2.21 (s, 3H), 1.95 (s, 3H).

$^{13}\text{C}$ NMR (125 MHz, DMSO- $d_6$ ):  $\delta = 169.04, 152.99, 139.48, 134.93, 132.22, 129.04, 128.45, 128.42, 126.15, 125.90, 122.26, 118.91, 118.38, 47.52, 22.59, 20.46.$

*N*-((2-hydroxynaphthalen-1-yl) (4-hydroxyphenyl) methyl) acetamide (**2e**)

$^1\text{H}$ NMR (500 MHz, DMSO- $d_6$ ):  $\delta = 9.91$  (s, 1H), 9.16 (s, 1H), 8.35 (m, 1H), 7.77 (m, 3H), 7.34 (s, 1H), 7.21 (m, 2H), 6.98 (m, 3H), 6.62 (m, 2H), 1.93 (s, 3H).

$^{13}\text{C}$ NMR (125 MHz, DMSO- $d_6$ ):  $\delta = 169.40, 156.18, 153.48, 133.04, 132.80, 129.42, 128.94, 127.74, 126.63, 123.83, 122.79, 119.64, 119.02, 115.24, 115.16, 48.04, 23.19.$

*N*-((2-hydroxynaphthalen-1-yl) (3-nitrophenyl) methyl) acetamide (**2f**)

$^1\text{H}$ NMR (500 MHz, DMSO- $d_6$ ):  $\delta = 10.12$  (s, 1H), 8.62 (s, 1H), 8.02 (m, 2H), 7.81 (m, 3H), 7.55 (m, 2H), 7.40 (m, 1H), 7.22 (m, 3H), 2.02 (s, 3H).

$^{13}\text{C}$ NMR (125 MHz, DMSO- $d_6$ ):  $\delta = 170.17, 153.38, 148.23, 133.33, 132.65, 130.83, 130.37, 130.03, 129.17, 128.89, 127.25, 123.25, 123.10, 121.70, 120.92, 118.94, 118.31, 48.13, 22.73.$

*N*-((2-hydroxynaphthalen-1-yl) (phenyl) methyl) acetamide (**2g**)

$^1\text{H}$ NMR (500 MHz, DMSO- $d_6$ ):  $\delta = 9.94$  (s, 1H), 8.40 (s, 1H), 7.72 (m, 3H), 7.34 (s, 1H), 7.19 (m, 7H), 1.98 (3H).

$^{13}\text{C}$ NMR (125 MHz, DMSO- $d_6$ ):  $\delta = 169.62, 153.56, 143.03, 132.75, 129.63, 128.94, 128.37, 126.71, 126.46, 123.67, 122.79, 119.29, 118.89, 48.26, 23.08.$

*N*-((2-hydroxynaphthalen-1-yl) (4-nitrophenyl) methyl) acetamide (**2h**)

$^1\text{H}$ NMR (500 MHz, DMSO- $d_6$ ):  $\delta = 10.2$  (s, 1H), 8.6 (d,  $J = 6.5$ , 1H), 8.11 (m, 2H), 7.79 (m, 3H), 7.34 (m, 3H), 7.27 (m, 1H), 7.20 (d,  $J = 8.1$ , 1H), 2.00 (s, 3H).

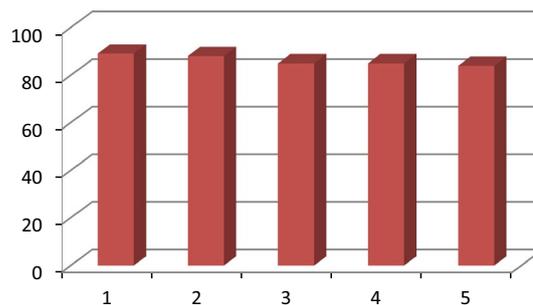
$^{13}\text{C}$ NMR (125 MHz, DMSO- $d_6$ ):  $\delta = 169.56, 151.17, 145.84, 132.13, 129.75, 128.57, 128.29, 127.06, 126.60, 123.13, 122.75, 122.43, 118.42, 117.73, 47.84, 22.46.$

The catalytic activity and the ability of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  to be recycled and reused are studied (Fig. 5). The catalyst is separated by an external magnet and is reused as such for subsequent experiments under similar reaction conditions. Yields of the product decrease only slightly after five attempts.

A comparison for the efficiency of the catalytic activity of  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  is made with six other methods (Table 3). The results show that this method is superior to some of the earlier methods in terms of yields and reaction times.

## Conclusion

Covalent functionalization of  $\text{AlCl}_3$  onto the magnetic  $\text{Fe}_2\text{O}_3$  nanoparticles is successfully achieved by a multiple



**Fig. 5** Reusability of the  $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2\text{-AlCl}_2$  catalyst

**Table 3** Comparison of catalytic activity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-AlCl<sub>3</sub> with known catalysts

Entry <sup>a</sup>	Catalyst	Condition	Time	Yield <sup>b</sup> (%)	Reference
1	Montmorillonite K10 clay	Solvent-free/125 °C	1.5 h	89	[18]
2	<i>p</i> -TSA	Solvent-free/125 °C	5 h	88	[27]
3	Copper <i>p</i> -toluenesulfonate	Solvent-free/80 °C	1.5 h	94	[28]
4	K <sub>5</sub> CoW <sub>12</sub> O <sub>40</sub> ·3H <sub>2</sub> O	Solvent-free/125 °C	2 h	90	[18]
5	Thiamine HCl (0.5 mmol)	Solvent-free/80 °C	4 h	88	[29]
6	I <sub>2</sub> (5 mol %)	Solvent-free/125 °C	15 h	89	[15]
7	Wet-cyunaric chloride	Solvent-free/ 100 °C	10 min	91	[17]
8	Zwitterionic salt	Solvent-free/80 °C	2 h	80	[32]
9	H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	Solvent-free/110 °C	20 min	92	[33]
10	Zeolite H-BEA	Solvent-free/120 °C	5–7 min	85	[34]
11	H <sub>3</sub> BO <sub>3</sub>	Solvent-free/120 °C	15 min	73	[35]
12	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> -AlCl <sub>3</sub>	Solvent-free/120 °C	10 min	89	—

<sup>a</sup> Benzaldehyde (1 mmol), acetamide (1.2 mmol), 2-naphthol (1 mmol), catalyst, 120 °C

<sup>b</sup> Isolated yield

synthetic procedure which is confirmed with XRD, ICP, TGA, and SEM. The most interesting features of the present work include durability as well as efficient catalytic activity for one-pot synthesis of amidoalkyl naphthols via three-component solvent free coupling reactions of aldehydes, amides, and 2-naphthol. This method offers several advantages including high yield, short reaction time, simple work-up procedure, ease of separation, and recyclability of the magnetic catalyst, as well as the ability to tolerate a wide variety of substitutions in the reagents.

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