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Fabrication, identification and application of Fe_3O_4 bonded nicotinic acid-sulfonic acid chloride as a retrievable magnetic nanostructured catalyst for the one-pot synthesis of 1-carbamato-alkyl-2-naphthols

Ardeshir Khazaei[1] · Mahsa Tavasoli[1] · Ahmad Reza Moosavi-Zare[2]

Abstract In the presented work, Fe_3O_4 bonded nicotinic acid-sulfonic acid chloride (Fe_3O_4@nicotinic acid @sulfonic acid chloride), as a magnetic reusable catalyst, was prepared by a simple procedure. The identification of Fe_3O_4@nicotinic acid @sulfonic acid chloride was studied by Fourier transform infrared spectroscopy, X-ray diffraction, thermal gravimetric analysis, scanning electron microscopy, energy dispersive X-ray analysis and vibrating sample magnetometry. Fe_3O_4@nicotinic acid @sulfonic acid chloride was employed as an efficient and heterogeneous catalyst for the one-pot synthesis of some 1-carbamato-alkyl-2-naphthol derivatives in high yields under solvent-free conditions. Simple work up, high yields, short reaction times and easy recovery of catalyst are some advantages of this work.
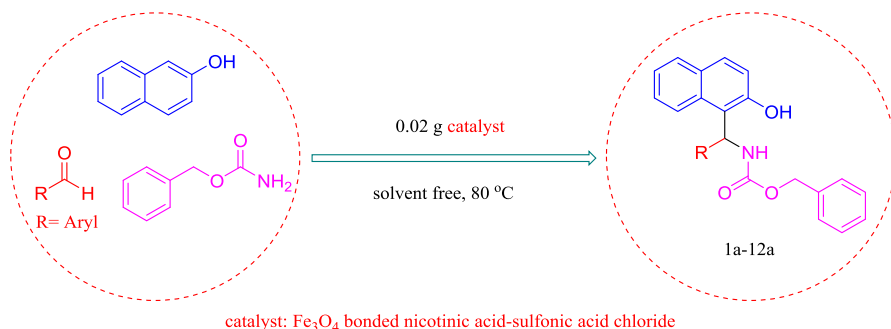
✉ Ardeshir Khazaei
Khazaei_1326@yahoo.com

1 Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran

2 Department of Chemistry, Sayyed Jamaleddin Asadabadi University, Asadabad 6541861841, Iran

Graphical Abstract

catalyst: Fe$_3$O$_4$ bonded nicotinic acid-sulfonic acid chloride

Keywords Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride · Fe$_3$O$_4$ nanoparticle · 1-Carbamato-alkyl-2-naphthol · Solvent-free

Introduction

Nanoparticles are widely used in various pharmaceutical and electronic industries and in the coloring industry due to their different sizes, shapes and materials. Today, the application of nanoparticles has been much considered in catalytic applications. Nanoparticles are desirable substrates to replace homogeneous catalysts. When the size of the substrate is decreased to nanoscale, the surface-to-volume ratio is increased. As a result, the activity of stabilized catalysts on nanoparticles increases because of the interaction of these catalysts with high availability surfaces [1–3]. However, the easy separation and recovery of nano-catalysts from the reaction environment is still a challenge. Previous reported techniques such as straightening are not effective for separating these catalysts due to nanoscale particle size. It involves high cost, long time spent, and the use of special separation techniques such as centrifugation and chromatography.

In this case, Fe$_3$O$_4$ nanoparticles have been used as an efficient solid support for catalysts; due to their insoluble and magnetic properties. In addition, the separation of these compounds from the reaction mixture can be easily done with an external magnet, where the catalysis filtration is not necessary [4–9].

Recently, most of the chemists are interested in synthesis of organic compounds using multi component reactions (MCRs). Some advantages of this method are as follows: Preparing target compounds with high atomic economy and more efficiency by the reaction of three or more compounds together in one pot, increasing simplicity and synthetic efficiency of the conventional organic transformations [10–16].

1-Carbamato-alkyl-2-naphthols are interesting for chemists because of the biological activities of these compounds. The derivatives of these compounds have hypotensive and bradycardic effects [17, 18]. Many catalysts have been reported for the preparation of 1-carbamato-alkyl-2-naphthols by one-pot synthesis between

alkyl carbamates, 2-naphthol and various aromatic aldehydes [19–29]. Some of these catalysts have some disadvantages such as hard reaction conditions, long reaction times, low yields, use of corrosive and expensive materials, boring work up and high reaction temperature. Having the above facts, finding an efficient method is still needed.

Herein, we have introduced Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride nanoparticles as a highly active catalyst for the one-pot synthesis of 1-carbamato-alkyl-2-naphthols (Scheme 1). Mild and solvent-free conditions, reusable processes, simple operation, short reaction times, easy recovery, and high yields are some advantages of this work. The separation of Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride from reaction mixture was done by an external magnet and reused for four times without a significant decrease of the yield.

Experimental

Materials and methods

All of the starting materials and solvents that have been used in this research were purchased from the Merck Company and were applied without any further purification. Fourier transform infrared (FT-IR) spectra were recorded using KBr Pill on a Perkin-Elmer Spectrum 65 .A FT-IR spectrometer in the range of 400–4000 cm^{-1} was used in order to identify the functional groups in synthesized materials. The ^{1}H NMR and ^{13}C-NMR spectrums of synthesized products were identified by 250 MHz Bruker Avance, Switzerland. The determination of the melting points was done on Büchi B-545 melting points equipment. The crystalline structure of synthesized catalyst was investigated by X-ray diffraction (XRD) using an Ital structure APD 2000 with Cu Kα radiation in the 2θ range of 10.5–90° at ambient temperature. Thermal gravimetric analysis (TGA) was reported in the temperature range of 30–600 °C under nitrogen atmosphere and on a Perkin Elmer instrument (Model: Pyris 1). It should be noted that the rate of increase in the temperature is 10 °C/min in this apparatus. To provide elemental identification and quantitative compositional information of catalyst, the EDX was done using an Oxford scanning electron microscope instrument. To investigate the surface morphology of nano-catalyst, FE-SEM was carried out on a SIGMA VP-500
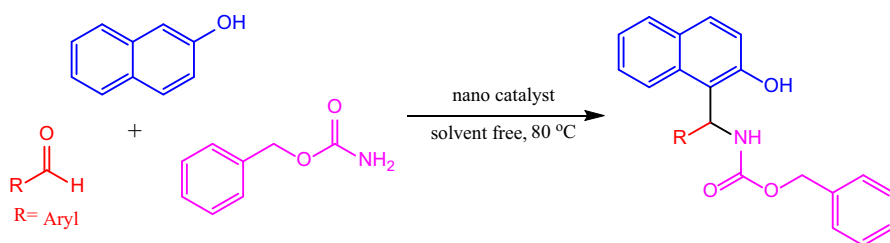
Scheme 1 The preparation of 1-carbamato-alkyl-2-naphthols by nano catalyst

(ZEISS) instrument. The measurement of super magnetic properties of catalyst was performed using a vibrating sample magnetometer (MDKB instrument).

Synthesis of nano Fe_3O_4@Nicotinic acid

Fe_3O_4@Nicotinic acid was prepared using the previous method [30] as follows: In a three-necked round-bottom flask, $FeCl_3 \cdot 6H_2O$ (0.0216 mol, 5.89 g), $FeCl_2 \cdot 4H_2O$ (0.011 mol, 2.17 g) and nicotinic acid (0.043 mol, 5.29 g) were dissolved in 100 mL of distilled water at room temperature. The homogeneous solution is stirred using a magnetic stirrer under nitrogen atmosphere at 60 °C for 30 min. Then, by adding 25% solution of NH_3 (15 mL) to this mixture, a black colored suspension appeared. Then the mixture was refluxed under N_2 atmosphere at 90 °C for 6 h. In the end, the resulting black precipitate was separated by an external magnetic field, and it was washed with distilled water for five times. The obtained nanoparticles were dried at 60 °C for 12 h.

Synthesis of Fe_3O_4@nicotinic acid @sulfonic acid chloride nanoparticles

Nano Fe_3O_4@Nicotinic acid (0.5 g) was added to 6 mL of dry dichloromethane (under sonication for 30 min) and then added slowly in a 50 mL round-bottomed flask containing a solution of chlorosulfonic acid (15 mmol) in dichloromethane (10 mL) and stirred for 3 h. Then, a brown powder was separated by a permanent magnet, washed thoroughly with dichloromethane for several times and dried at 60 °C for 12 h.

General procedure for solvent free synthesis of 1-carbamato-alkyl-2-naphthols

A mixture of 2-naphthol (2.0 mmol), benzyl carbamate (2.2 mmol), aromatic aldehyde (2.0 mmol) and Fe_3O_4@nicotinic acid @sulfonic acid chloride nanoparticles (0.02 g) as a nanostructured magnetic catalyst was stirred magnetically at 80 °C in an oil bath for an appropriate time. The completion of the reaction was monitored by TLC. Hot ethyl acetate was added to reaction vessel in order to dissolve the reaction mixture. The catalyst was separated easily by an external magnet. After recrystallization, pure crystals of 1-carbamato-alkyl-2- naphthol derivatives were obtained. The products were identified by spectral and physical data. The recovered catalyst was washed with hot ethyl acetate for several times, and dried to reuse for another reaction. The recovered catalyst was used again for four times on the synthesis of 1-carbamato-alkyl-2-naphthol derivatives without a significant decrease in the yield of products. The obtained products were identified by ^1H NMR, ^{13}C NMR and FT-IR analysis.

Analytical data of selected products

*Benzyl ((2-hydroxynaphthalen-1-yl)(phenyl)methyl)carbamate (**1a**)*

M. P. 185–187 °C. IR (KBr, v, cm^{-1}): 3424, 3210, 3067, 1676, 1631, 1516, 1439, 1328, 1271, 1229, 1131, 1041, 944, 808, 753, 697; ^{1}HNMR (250 MHz DMSO-d_6, δ, ppm): δ 5.046 (*s*, 2H, CH$_2$), 6.881 (*s*, 1H, CH), 7.218–7.767 (*m*, 16H, ArH), 7.882 (*s*, 1H, NH,), 10.111 (s,1H,OH); ^{13}CNMR (62.9 MHz DMSO-d_6, δ, ppm): 50.858, 66.131, 118.888, 119.249, 122.960, 123.530, 126.446, 126.814, 126.950, 128.221, 128.545, 128.772, 129.001, 129.777, 132.489, 137.425, 142.758, 153.341, 156.491.

*Benzyl ((3-chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)carbamate (**2a**)*

M. P. 182–186 °C. IR (KBr, v, cm^{-1}): 3436, 3245, 3069, 1675, 1629, 1596, 1508, 1439, 1328, 1272, 1228, 1066, 948, 892, 813, 702; ^{1}HNMR (250 MHz DMSO-d_6, δ, ppm): δ 5.023 (*d*, 1H, CH, J = 12.5 Hz), 5.104 (*d*, 1H, CH, J = 12.5 Hz) 6.89 (*d*, 1H, CH, J = 7.75 Hz), 7.150–7.779 (*m*, 15H, ArH), 7.894 (*s*, 1H, NH), 10.189 (*s*, 1H, OH); ^{13}CNMR (62.9 MHz DMSO-d_6, δ, ppm): 50.489, 66.228, 118.648, 118.864, 123.060, 123.341, 125.246, 126.201, 126.818, 127.149, 128.233, 128.777, 129.080, 130.114, 130.463, 132.378, 133.367, 137.373, 145.521, 153.462, 156.548.

*Benzyl ((2,4-dichlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)carbamate (**3a**)*

M. P. 205–207 °C. IR (KBr, v, cm^{-1}): 3417, 3344, 3069, 1686, 1628, 1585, 1513, 1436, 1341, 1271, 1244, 1054, 845, 820, 744; ^{1}HNMR (250 MHz DMSO-d_6, δ, ppm): δ 5.011(*s*, 2H, CH$_2$), 6.810 (*s*, 1H, CH), 7.074–7.747 (*m*, 14H, ArH), 7.965–8.053 (*d*, 1H, NH, J = 22 Hz), 9.899 (*s*, 1H,OH); ^{13}CNMR (62.9 MHz DMSO-d_6, δ, ppm): 49.893, 65.885, 116.671, 118.982, 122.833, 123.096, 126.918, 127.075, 127.905, 128.137, 128.712, 129.020, 129.081, 130.178, 131.666, 132.416, 132.998, 133.619, 137.532, 139.209, 154.016, 156.070.

*Benzyl ((2-hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl)carbamate (**4a**)*

M. P. 201–203 °C. IR (KBr, v, cm^{-1}): 3414, 3306, 3064, 1697, 1630, 1528, 1516, 1441, 1347, 1281, 1048, 811, 696; ^{1}HNMR (250 MHz DMSO-d_6, δ, ppm): δ 5.03(*d*, 1H, CH, J = 12.5 Hz), 5.11 (*d*, 1H, CH, J = 12.5 Hz), 6.97 (*d*, 1H, CH, J = 8.25 Hz), 7.185–8.053 (*m*, 15H, ArH), 8.121 (*s*, 1H, NH), 10.241 (*s*, 1H, OH); ^{13}CNMR (62.9 MHz DMSO-d_6, δ, ppm): 50.497, 66.278, 118.236, 118.838, 120.944, 121.945, 123.129, 123.177, 127.287, 128.193, 128.261, 128.790, 129.130, 130.138, 130.395, 132.340, 133.259, 137.322, 145.428, 148.197, 153.601, 156.641.

*Benzyl ((2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl)carbamate (**5a**)*

M. P. 203–205 °C. IR (KBr, v, cm^{-1}): 3411, 3306, 3064, 1687, 1628, 1606, 1515, 1347, 1276, 1238, 1049, 852, 824, 745; ^{1}HNMR (250 MHz DMSO-d_6, δ, ppm): δ 5.070 (*t*, 2H, CH$_2$), 6.97 (*d*, 1H, CH, J = 7.75 Hz), 7.194–7.963 (*m*, 15H, ArH), 8.11

(*d*, 1H, NH, *J* = 7.75 Hz), 10.195 (*s*, 1H, OH); ^{13}CNMR (62.9 MHz DMSO-d_6, δ, ppm): 50.724, 66.329, 118.349, 118.820, 123.089, 123.268, 123.762, 127.226, 127.586, 128.248, 128.769, 129.095, 130.355, 132.361, 137.271, 146.529, 151.075, 153.571, 156.635.

Benzyl ((4-bromophenyl)(2-hydroxynaphthalen-1-yl)methyl)carbamate (8a)

M. P. 180–182 °C. FT-IR (KBr, *v*, cm^{-1}): 3425, 3196, 3069, 1682, 1628, 1517, 1486, 1329, 1273, 1069, 1009, 817, 748; ^{1}HNMR (250 MHz DMSO-d_6, δ, ppm): δ 5.00 (*d*, 1H, CH, *J* = 12.75 Hz), 5.07 (*d*, 1H, CH, *J* = 12.75 Hz), 6.831 (d, 1H, CH, *J* = 8.5 Hz), 7.128–7.801 (*m*, 15H, ArH), 7.843 (*s*, 1H, NH), 10.140 (*s*, 1H, OH); ^{13}CNMR (62.9 MHz DMSO-d_6, δ, ppm): 50.389, 66.183, 118.75, 118.830, 119.851, 123.002, 123.412, 127.038, 128.216, 128.733, 129.035, 129.990, 131.390, 132.364, 137.349, 142.311, 153.397, 156.485.

Results and discussion

Synthesis and identification of Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride

In this work, we report the fabrication of Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride nanoparticles, and its catalytic application on the synthesis of 1-carbamato-alkyl-2-naphthols. The structure of the catalyst was studied by IR, XRD, SEM, TGA, VSM and EDX analysis. According to the procedure that is shown in Scheme 2, the catalyst was synthesized in two steps. Firstly, Fe$_3$O$_4$@nicotinic acid was prepared by refluxing method of iron (**II**), iron (**III**) ions and nicotinic acid and then adding to an aqueous solution of ammonia. Secondly, Fe$_3$O$_4$@nicotinic acid was functionalized by ClSO$_3$H to produce Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride as reusable magnetic catalyst.

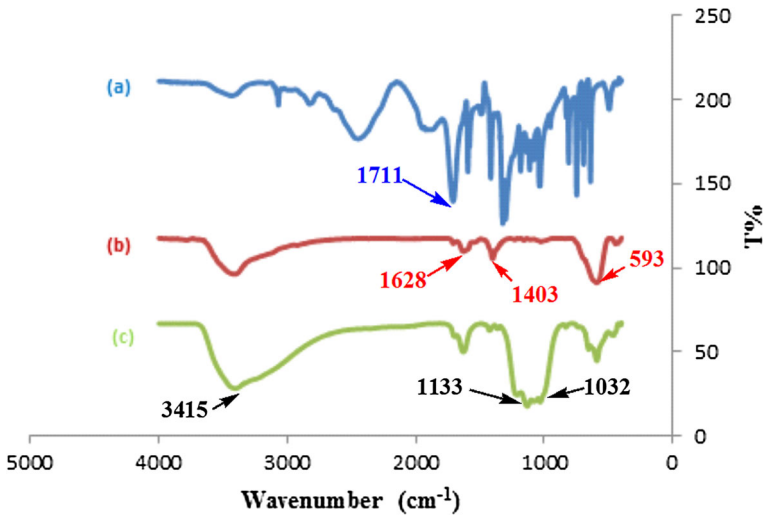The FT-IR spectra of the nicotinic acid (a), Fe$_3$O$_4$@nicotinic acid (b), and Fe$_3$O$_4$@ nicotinic acid @sulfonic acid chloride nanoparticles (c) were recorded and shown in Fig. 1. The comparison between FT-IR spectra of nicotinic acid, and Fe$_3$O$_4$@ nicotinic acid showed that the C=O stretching bond of the carboxyl group, which appeared at 1711 cm^{-1} in the pure nicotinic acid, was not present in the spectrum of Fe$_3$O$_4$@nicotinic acid because of the binding of the nicotinic acid to the surface of Fe$_3$O$_4$. In Fig. 1b, the observed peak at 1403 cm^{-1} is due to symmetrical connection of carboxylic acid oxygen atoms to the surface of Fe$_3$O$_4$ nanoparticles [31, 32] and also the peak that appeared at 1628 cm^{-1} corresponded to C=N vibration of the pyridine ring. Thus, Fe–O bond vibration of iron oxide at 593 cm^{-1} is shown in Fig. 1b. In the spectrum of Fe$_3$O$_4$@ nicotinic acid@ sulfonic acid chloride (c), the assigned peak at 3415 cm^{-1} was related to OH stretching of the SO$_3$H group. Additionally, spectrum (c) showed the bonds at 1032 and 1133 cm^{-1} correspond to N-SO$_2$ and O-SO$_2$ vibrations, respectively.

To investigate the crystalline nature and surface state of Fe$_3$O$_4$@ nicotinic acid@ sulfonic acid chloride nanoparticles, X-ray diffraction analysis (XRD) was studied
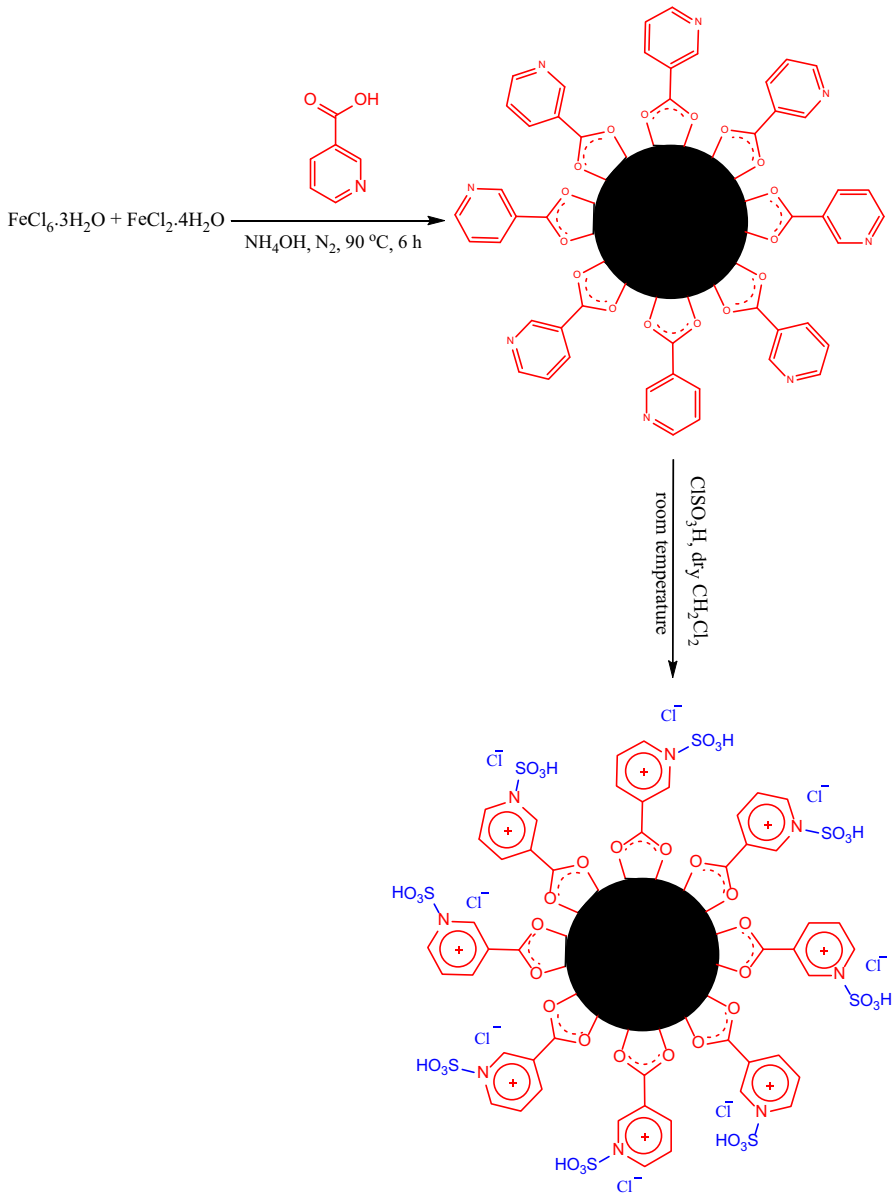
Scheme 2 The synthesis of Fe₃O₄@nicotinic acid @sulfonic acid chloride

in a domain of 10.5–90°, and the results are shown in Fig. 2. According to Scherer's formula, the size of the crystals is calculated from 15 to 90 nm. X-ray diffraction pattern and FT-IR spectrum of Fe₃O₄ in comparison with other species of the catalyst are given in the supporting information (Figures **S1** and **S2**).

Fig. 1 FT-IR spectra: *a* nicotinic acid; *b* Fe_3O_4@nicotinic acid; *c* Fe_3O_4@nicotinic acid @sulfonic acid chloride nanoparticles
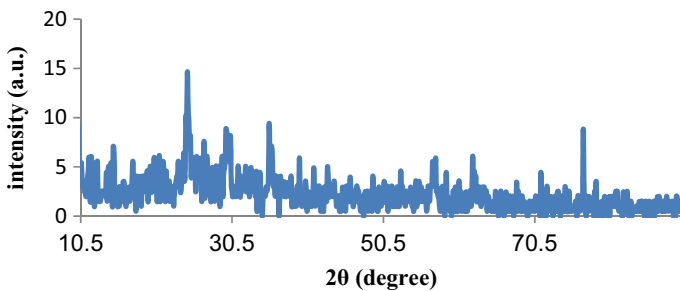
Fig. 2 X-ray diffraction pattern of Fe_3O_4@nicotinic acid @sulfonic acid chloride nanoparticles

Thermal gravimetric analysis (TGA) curves of Fe_3O_4@ nicotinic acid (a) and Fe_3O_4@ nicotinic acid@ sulfonic acid chloride (b) are shown in Fig. 3. According to Fig. 3a, the weight losses of Fe_3O_4@nicotinic acid was done in two steps. The first weight loss up to 100 °C could be related to exit solvent from the catalyst. The thermal decomposition of the organic moiety established on the Fe_3O_4 surface, appeared at 260–481 °C at about 5.5%. Also, the Fig. 3b shows a very severe weight loss in the range of 242–680 °C which represents the stability of the nano-catalyst in this temperature range.

The measurement of magnetic properties of Fe_3O_4@nicotinic acid (a), and Fe_3O_4@ nicotinic acid@ sulfonic acid chloride nanoparticles (b) was investigated by VSM at room temperature (Fig. 4). The evaluation of these two curves showed that the saturation magnetization was reduced from 55 to 12 emu g^{-1} due to the functionalization of nicotinic acid by $ClSO_3H$.
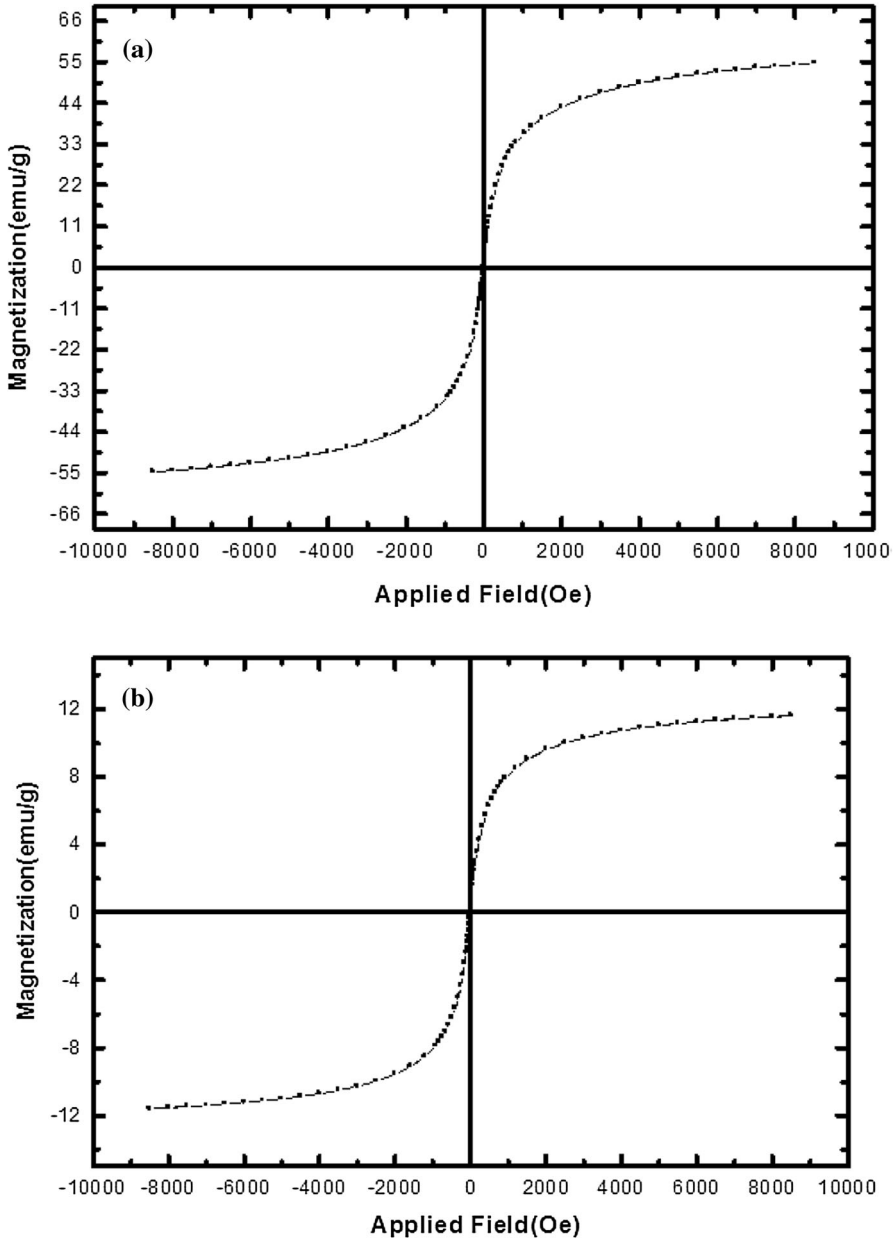
(a)

(b)
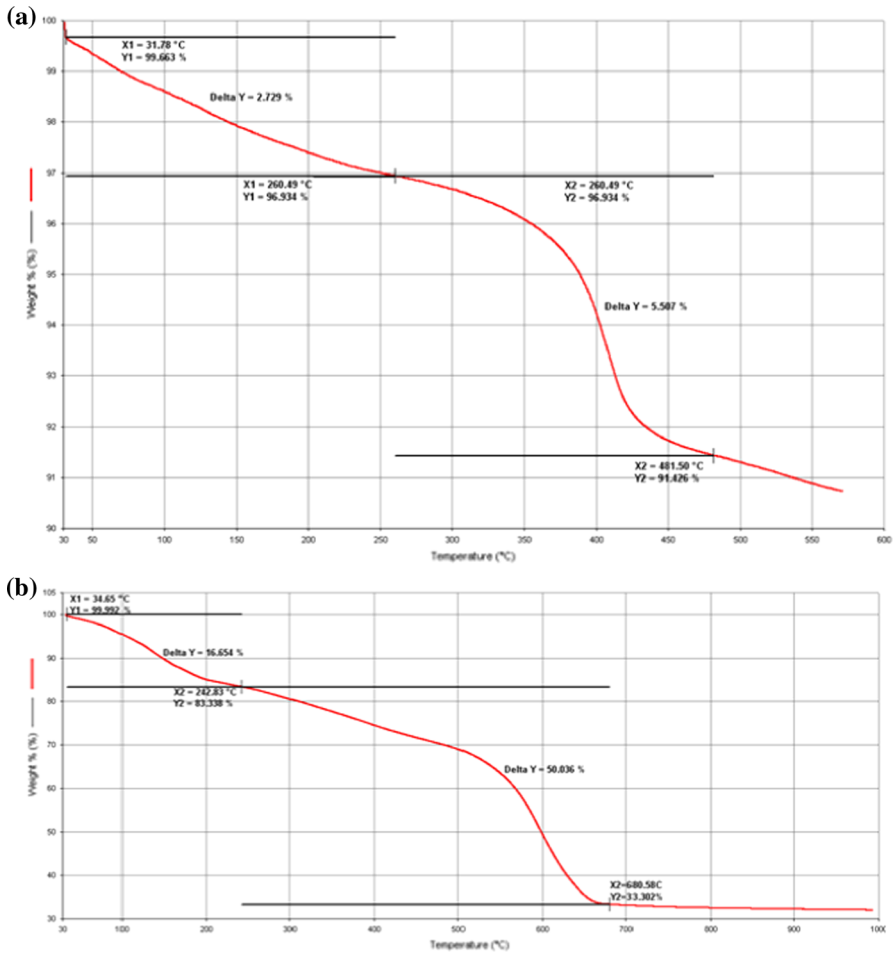
Fig. 3 The TG curves: **a** Fe_3O_4@nicotinic acid; **b** Fe_3O_4@nicotinic acid @sulfonic acid chloride nanoparticles

The presence of elements such as carbon (C), nitrogen (N), oxygen (O), sulfur (S), chlorine (Cl) and iron (Fe) was confirmed by an energy-dispersive X-ray (EDX) spectrum (Fig. 5). The EDX data well demonstrated the synthesis of Fe_3O_4@ nicotinic acid@ sulfonic acid chloride nanoparticles.

The morphology and the size of the nanostructured catalyst were evaluated by SEM analysis. These results showed that Fe_3O_4@ nicotinic acid@ sulfonic acid chloride nanoparticles appeared uniform, and the size of them is between 11 and 34 nm (Fig. 6).

Fig. 4 Magnetization curves: **a** Fe₃O₄@Nicotinic acid; **b** Fe₃O₄@nicotinic acid @sulfonic acid chloride nanoparticles
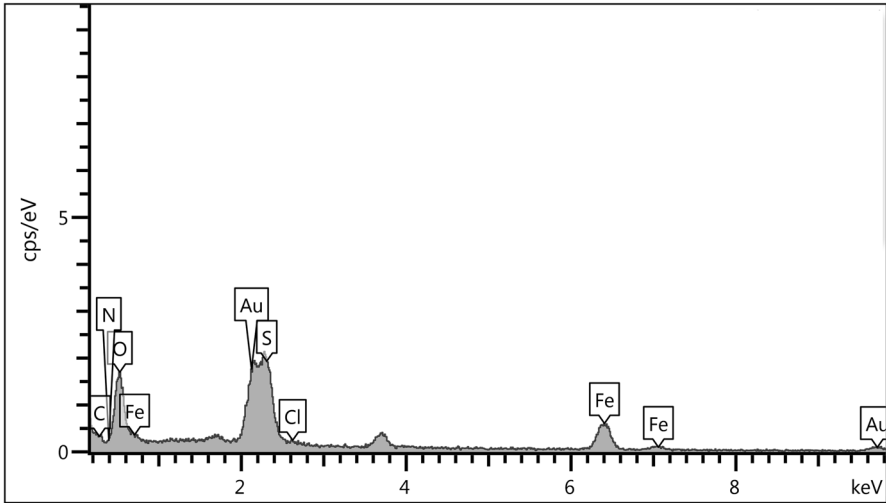
Fig. 5 EDX spectrum of Fe₃O₄@nicotinic acid @sulfonic acid chloride nanoparticles
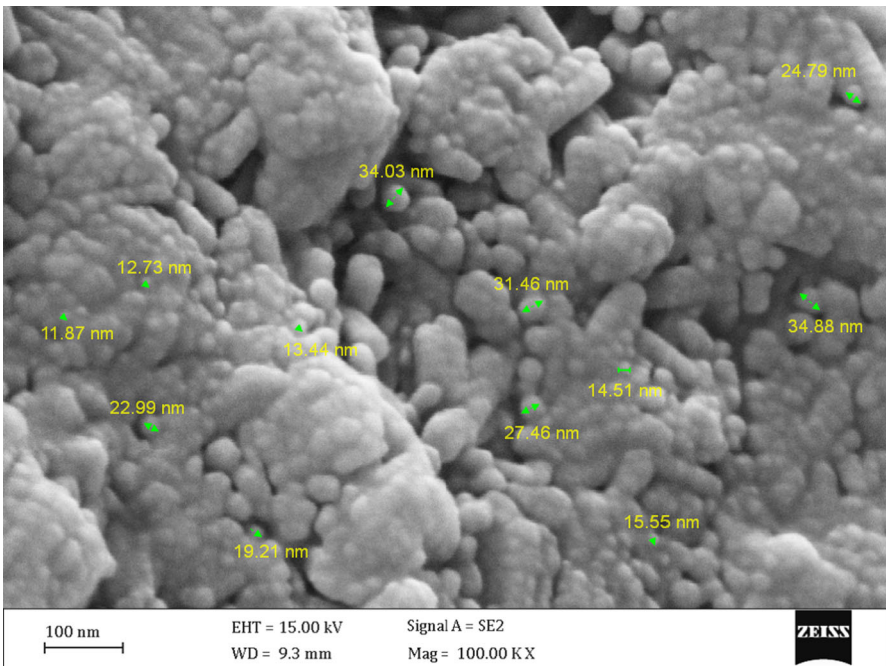
Fig. 6 SEM image of Fe₃O₄@nicotinic acid @sulfonic acid chloride nanoparticles

Catalytical application of Fe₃O₄ bonded nicotinic acid-sulfonic acid chloride

We have checked the efficacy of the catalyst for the synthesis of 1-carbamato-alkyl-2-naphthols. The reaction between benzyl carbamate, benzaldehyde and 2-naphthol undersolvent-free conditions was selected as a model reaction. At first, the reaction between benzyl carbamate, benzaldehyde and 2-naphthol was done in the absence of the catalyst over a period of 60 min, but the yield of product was low (Table 1, Entry 1). The high yield of product was obtained with 0.02 g of catalyst at 80 °C under solvent-free conditions (Table 1-Entry 6).

The comparisons between this catalyst and the other previous reported catalysts for the preparation of compound **1a** are depicted in Table 2. According to Table 2, the presented catalyst is more effective than the other reported catalysts in order to secure shorter reaction time, higher yield, more suitable temperature and easy recovery.

The generality of the catalyst was investigated by the reaction of various aromatic aldehydes with 2-naphthol and benzyl carbamate using 0.02 g of the catalyst under mild reaction conditions (Table 3). The synthesis of 1-carbamato-alkyl-2-naphthol derivatives with different aldehydes in the presence of Fe_3O_4@ nicotinic acid@ sulfonic acid chloride had good and acceptable results.

According to previous literature [20, 22, 24, 28, 29], we suggest a possible mechanism for the synthesis of 1-carbamato-alkyl-2-naphthols catalyzed by Fe_3O_4@ nicotinic acid@ sulfonic acid chloride nanoparticles (Scheme 3). In the initial step, the intermediate (**A**) was formed by the reaction of 2-naphthol with an activated aldehyde by the catalyst. Then, by leaving one molecule of H_2O from the intermediate (**A**), ortho-quinone methide (*o*-QM) (**B**) was prepared. Finally, the

Table 1 Effect of different amounts of the catalyst and temperature on the reaction of benzaldehyde (2 mmol), benzyl carbamate (2.2 mmol) and 2-naphthol (2 mmol) in the absence of solvent

Entry	Catalyst (mol%)	Temperature (°C)	Time (min)	Yield (%)[a]
1	–	80	60	Trace
2	0.001	80	15	40
3	0.005	80	15	50
4	0.007	80	12	55
5	0.01	80	8	65
6	0.02	80	4	88
7	0.03	80	4	85
8	0.05	80	4	89
9	0.02	rt	60	30
10	0.02	50	15	45
11	0.02	70	7	74
12	0.02	90	4	88
13	0.02	100	5	87

[a]Isolated yield

Table 2 Comparison result of Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride nanoparticles with other reported catalysts in the synthesis of compound **1a**

Entry	Catalyst	Temperature (°C)	Time (min)	Yield (%)[b]	References
1	Al(MS)$_3$·4H$_2$O	70	36	85	[19]
2	4-(1-Imidazolium) butanesulfonate	80	120	75	[20]
3	NaHSO$_4$/SiO$_2$	100	10	75	[22]
4	Mg(OOCCF$_3$)$_2$	100	20	81	[25]
5	Tween®20	75–80	50	89	[26]
6	Fe$_3$O$_4$@ nicotinic acid@ sulfonic acid chloride	80	4	88	–[c]

[a]Reaction condition: benzaldehyde (2 mmol), benzyl carbamate (2.2 mmol) and 2-naphthol (2 mmol), solvent free

[b]Isolated yield

[c]This work

desired 1-carbamato-alkyl-2-naphthol was prepared by the Michael reaction between benzyl carbamate and orthoquinone methide.
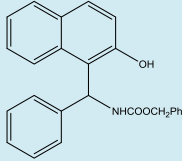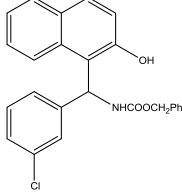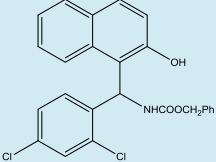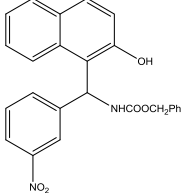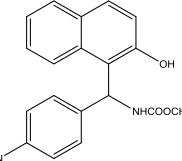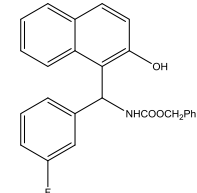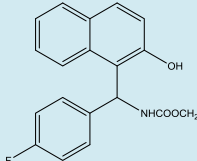
Recovery and reusability of nano-catalyst

To investigate the stability of the catalyst, the reaction between benzaldehyde (2 mmol), benzyl carbamate (2.2 mmol) and 2-naphthol (2 mmol) was studied as a model reaction using 0.02 g catalyst at 80 °C under solvent-free conditions. After completion of the reaction, hot ethyl acetate was added to the reaction mixture and stirred for 5 min. Then, the catalyst was easily separated by the external magnet. The separated catalyst was washed with hot ethyl acetate for several times, dried and reused for another reaction. The catalyst was successfully reused for four times without any remarkable reducing of catalytic activity (Fig. 7). The FT-IR spectrum of a reused catalyst was compared with fresh catalyst for which they have high compliance with each other (Fig. 8).
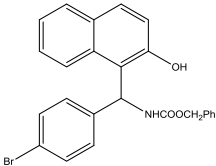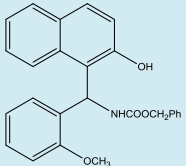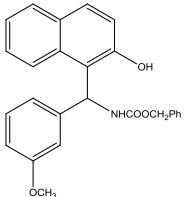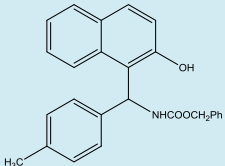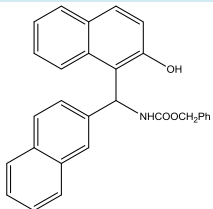
Conclusions

In this study, we have synthesized Fe$_3$O$_4$ bonded nicotinic acid-sulfonic acid chloride (Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride) as a novel heterogeneous catalyst and fully characterized by various techniques. The catalytic activity of this catalyst was checked by the one-pot synthesis of 1-carbamato-alkyl-2-naphthol derivatives under solvent-free conditions. This work showed notable advantages such as short reaction times, high yields, easily separation and retrievable of the catalyst.

Table 3 The solvent-free preparation of 1-carbamato-alkyl-2-naphthols from aromatic aldehydes benzyl carbamate, and 2-naphthol using Fe_3O_4@nicotinic acid @sulfonic acid chloride nanoparticles

Entry	Product	Time (min)	Yield (%)[b]	M. P. °C (Lit.)
1a		4	88	185-187 (180-182) [21]
2a		3	89	182-186 (185-187) [33]
3a		5	90	205-207 (208-210) [19]
4a		3	92	201-203 (200-202) [15]
5a		3	91	203-205 (200-204) [19]
6a		5	87	209-210 (208-210) [33]
7a		4	89	209-211 (209-210) [33]

Table 3 continued

Entry	Product	Time (min)	Yield (%)[b]	M. P. °C (Lit.)
8a		4	91	180-182 (180-181) [33]
9a		8	84	202-203 (202-203) [33]
10a		7	83	180-183 (182-184) [22]
11a		13	75	154-156 (152-154) [18]
12a		7	85	211-213 (210-211) [33]

Reaction conditions: aldehydes (2 mmol), benzyl carbamate (2.2 mmol), 2-naphthol (2 mmol), Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride nanoparticles (0.02 g), solvent-free, 80 °C
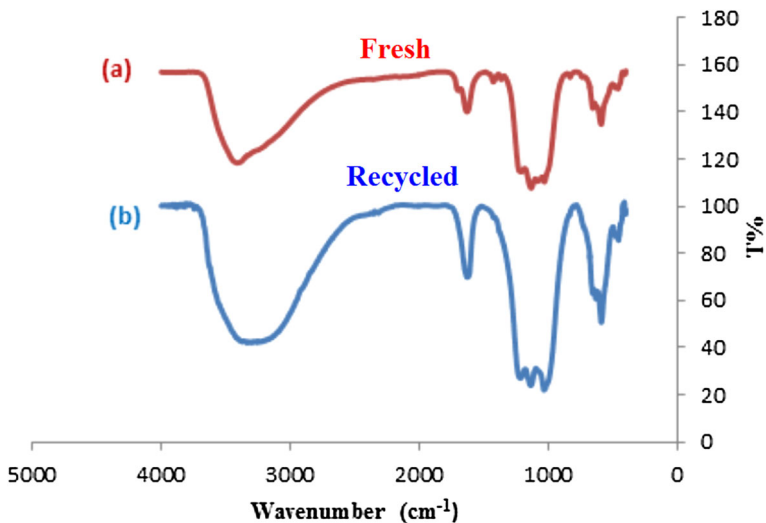
[a]Isolated yield
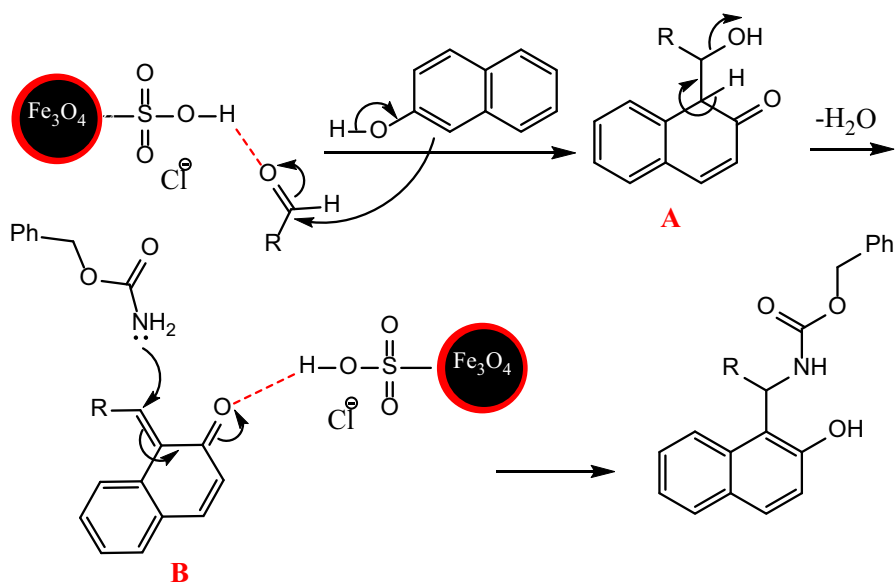
Scheme 3 The plausible mechanism for the synthesis of 1-carbamato-alkyl-2-naphthols catalyzed by Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride nanoparticles
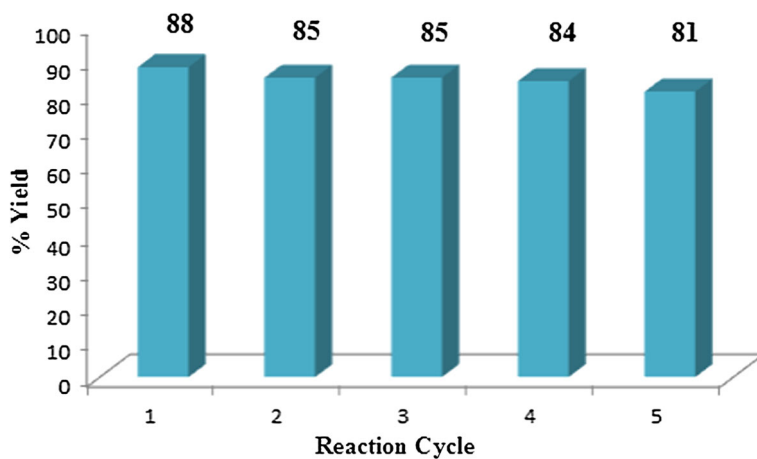
Fig. 7 Reusability test of the Fe$_3$O$_4$@nicotinic acid @sulfonic acid chloride nanoparticles

Fig. 8 FT-IR spectra: *a* fresh catalyst; *b* recovered catalyst

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