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FULL PAPER

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N-(3-silyl propyl) diethylene triamine *N*,*N*′,*N*″-tri-sulfonic acid immobilized on $Fe_{3\text{-}x}Ti_xO_4$ magnetic nanoparticles: A new recyclable heterogeneous nanocatalyst for the synthesis of hexahydroquinolines

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In the present study, for the first time *N*-(3-silyl propyl) diethylene triamine *N,N′,N″*-tri-sulfonic acid (SPDETATSA) was grafted on magnetic $Fe_{3\text{-}x}Ti_xO_4$ nanoparticles. The structure of the resulted nanoparticles was characterized based on Fourier-transform infrared (FT-IR), energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), and vibrating sample magnetometer (VSM) analyses. The results confirmed the successful immobilization of sulfamic acid groups onto the magnetic support. These nanoparticles exhibited high catalytic activity as novel magnetically recyclable acid nanocatalyst in the synthesis of a diverse range of hexahydroquinolines through one-pot tandem reactions in excellent yields. Also, this nanocatalyst performed satisfactory catalytic maintenance of activity for the synthesis of the reaction products after 4 rounds of recycling with no considerable loss of activity.

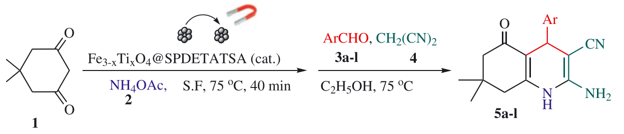
KEYWORDS
hexahydroquinolines, magnetic catalyst, nanocatalyst, sulfamic acid, titanomagnetite

1 | INTRODUCTION

Over the last decade, green chemistry has emerged as an important environmental issue in synthetic and industrial chemistry for environmental protection involving the use of eco-friendly reagents and catalysts, selected green media such as water, or solvent-free and non-classical ultrasound- or microwave-activated techniques[1,2] In terms of green chemistry, the development and application of enhanced and efficient processes such as multi-component reactions (MCRs) under benign conditions with using recyclable catalysts has become an important worldwide research challenge.[3–6] In this context, a great attention has been directed towards the preparation of supported heterogeneous catalysts by immobilizing the homogeneous precursors onto solid supports. In recent years, a variety of nanoparticles have been known as efficient catalysts and supports for immobilization of various homogeneous catalysts.[7–9] In general, immobilized catalysts have many outstanding characteristics including easy separation, air and moisture resistance, nontoxicity, high surface area, and reusability. Such properties make the immobilized catalysts superior over their non-supported counterparts.[10–14] However, many of these nanoparticles suffer from difficult and tedious separation by filtration or centrifugation.[15] To overcome this drawback, considerable efforts have been made for the synthesis and use of magnetic nanoparticles (MNPs), specially, magnetic nano-metal oxides,[16] as excellent supports for various catalysts,[17–22] which can be easily separated and recycled simply by using an external magnet.[23] Magnetic nanoparticles owing to their attractive properties, have been used as excellent support materials for preparation of MNP-supported heterogeneous catalysts which have found wide applications in traditional metal catalysis,[24–29] organocatalysis,[30] enzyme catalysis,[31] and industrial applications as well.[32] Fe_2O_3 and Fe_3O_4 nanoparticles are the most extensively studied as the core magnetic supports,[22,33] because of their high surface-area resulting in high catalyst loading capacity, conductivity, magnetic susceptibility, catalytic activity and striking stability.[34,35]

Quinolines have been of considerable interest owing to their broad variety of biological activities including antibacterial, antiasthmatic, antihypertensive, antimalarial, antiplatelet, and tyro kinase PDGF-RTK inhibiting properties.[36–41] In addition, 1,4-dihydopyridine containing quinolines are used as the most popular drugs as calcium channel blockers and also can cure the disordered heart ratio as chain-cutting agents of factor IV channel.[42,43]

Herein, we report for the first time the synthesis (Scheme 1) and characterization of *N*-(3-silyl propyl) diethylene triamine *N,N',N''*-tri-sulfonic acid immobilized on $Fe_{3-x}Ti_xO_4$ magnetic nanoparticles. Furthermore, we report the use of this magnetic catalyst as an efficient, heterogeneous and recyclable catalyst for the synthesis of hexahydroquinolines in one-pot tandem reactions between dimedone, ammonium acetate, aryl aldehydes and malononitrile (Scheme 2).



SCHEME 2 Synthesis of hexahydroquinolines **5a–l** via one-pot tandem reaction catalyzed by $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs

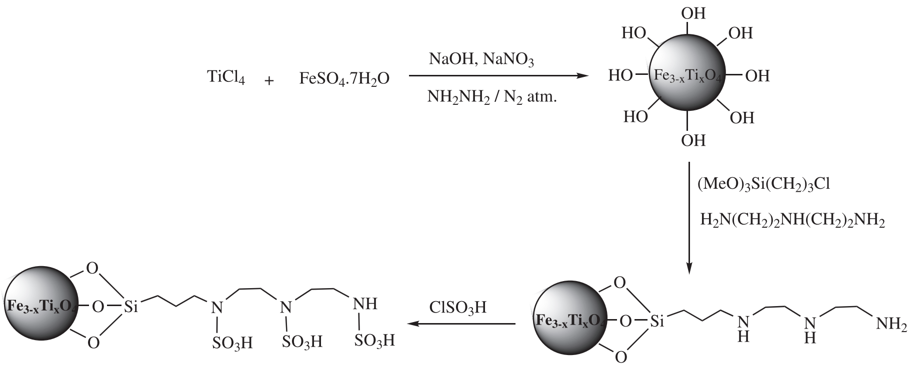
2 | EXPERIMENTAL

2.1 | General

Chemicals were purchased from Merck chemical company and used without further purification. Melting points were measured in open capillary tubes using a Stuart melting point SMP1 apparatus. Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets using a PerkinElmer Spectrum 65 FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on 90 and 250 MHz BRUKER AVANCE instruments for samples in DSMO-d_6 as solvent at ambient temperature. Mass spectra were recorded on an Agilent Technologies (5975C VL MSD with Tripe-Axis Detector) mass spectrometer operating at 70 eV. High resolution transmission electron microscopy (HRTEM Philips CM30, (300KV)) was also used to obtain TEM image. Scanning electron microscopy (SEM) images were obtained on a KYKY-EM3200 instrument operated at 26 kV accelerating voltage. Energy-dispersive X-ray (EDX) analysis of the prepared catalyst was performed on a FESEM-TESCAN MIRA3-FEG instrument. The curves obtained from thermo gravimetric analysis (TGA) were recorded under air atmosphere using TGA/DTA Linseis-181a1750 (Germany). Magnetic property of the sample was measured with a vibrating sample magnetometer (VSM, MDKFT, Iran) at room temperature. Ultrasonication was performed in a 2200 ETH-SONICA ultrasound cleaner at a frequency of 45 MHz.

2.2 | Preparation of the magnetic $Fe_{3-x}Ti_xO_4$ nanoparticles (MNPs)

Titanomagnetite ($Fe_{3-x}Ti_xO_4$) nanoparticles were prepared following our previously reported procedure.[44] In a two-neck round bottom flask, $FeSO_4.7H_2O$ (1.903 g) was dissolved in deionised water (10 ml). The pH value of the solution was reduced to <1 by using 1 M HCl solution. Then, $TiCl_4$ (0.75 ml) and hydrazine monohydrate (2 ml) were added respectively to the reaction mixture. The resulted mixture was refluxed at 90°C under N_2 atmosphere for 30 min. The process was followed by dropwise addition of a solution



SCHEME 1 Preparation of $Fe_{3-x}Ti_xO_4$-supported *N*-(3-silyl propyl) diethylene triamine *N,N ,N* -tri-sulfonic acid nanoparticles ($Fe_{3-x}Ti_xO_4$@SPDETATSA)

of NaOH (1.6 g) and $NaNO_3$ (0.77 g) in deionised water (10 ml) under vigorous stirring at a rate of 500 rpm. Then, the resulted mixture was stirred for another 1 hour. After cooling the reaction mixture to room temperature, the precipitated titanomagnetite ($Fe_{3-x}Ti_xO_4$) nanoparticles were magnetically isolated using an external magnet, washed with water several times, and dried in air.

2.3 | Preparation of $Fe_{3-x}Ti_xO_4$ bonded *N*-(3-silyl propyl) diethylene triamine ($Fe_{3-x}Ti_xO_4$@SPDETA)

A mixture of the prepared $Fe_{3-x}Ti_xO_4$ MNPs (1.0 g) in dry toluene (30 mL) was ultrasonicated for 30 min. 3-Chloropropyltrimethoxysilane (2 ml) and diethylene triamine (1.5 ml) were respectively added to the stirring reaction mixture and the resulted mixture was refluxed under N_2 atmosphere for 24 h. Then, the resulted reaction mixture was eventually cooled to room temperature and the modified nanoparticles $Fe_{3-x}Ti_xO_4$@SPDETA were magnetically separated, washed several times with ethanol and dried in air.

2.4 | Preparation of $Fe_{3-x}Ti_xO_4$ bonded *N*-(3-silyl propyl) diethylene triamine *N,N′,N″*-tri-sulfonic acid ($Fe_{3-x}Ti_xO_4$@SPDETATSA)

In a flat bottom flask, 1 g of $Fe_{3-x}Ti_xO_4$@SPDETA MNPs prepared from previous step was added to CH_2Cl_2 (15 ml). The resulted mixture was ultrasonicated for 30 min. Then, chlorosulfonic acid (1.5 ml) was added dropwise to the reaction mixture very slowly during 3 h (to prevent possible agglomeration of nanoparticles) at room temperature under vigorous stirring at a rate of 500 rpm. After completion of the addition, the reaction mixture was stirred for another 1 hour. Finally, the prepared $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs were magnetically separated from the reaction mixture, washed consecutively with CH_2Cl_2 (2 × 5 mL) and EtOH (3 × 5 ml), and dried in air.

2.5 | Typical procedure for the synthesis of hexahydroquinoline derivatives

A mixture of dimedone (0.14 g, 1 mmol), ammonium acetate (0.116 g, 1.5 mmol) and $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs (0.04 g) in a sealed tube was stirred at 75°C for 40 min. Then, aldehyde (1 mmol) and malononitrile (0.066 g, 1 mmol) were added to the reaction mixture under stirring. After 5 minute, the reaction mixture was diluted with ethanol (1 ml) and stirred at 75°C for an appropriated time (Table 2). After completion of the reaction as monitored by TLC, the mixture was diluted with hot ethanol, and stirred to dissolve all deposited product. Then, the catalyst was isolated by an external magnet and the remaining supernatant was cooled to room temperature, diluted with water (30 mL), and stirred for 10 min. The precipitated product was filtered and washed with small amount of cold ethyl acetate. Recrystallization of the crude product from EtOH/H_2O (3:2) provided pure product. All the synthesized products (**5a–l**) were known compounds and were characterized based on their melting points and spectral (FT-IR, ^1H NMR, ^{13}C NMR and mass) data and compared with the reported corresponding data (Table 2).

2.6 | Selected data

2.6.1 | 2-Amino-7,7-dimethyl-5-oxo-4-(*p*-tolyl)-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5b)

Yellow solid; m.p. 291–294°C; FTIR (KBr) ν: 3392, 3328, 3225, 3046, 2961, 2194, 1660, 1623, 1602, 1478, 1369, 1270, 1146, 1040, 563 cm^{-1}; ^1H NMR (250 MHz, DMSO-d_6) δ: 0.87 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.91–2.47 (m, 7H, CH_2, CH_2, CH_3), 4.23 (s, 1H, CH), 5.68 (s, 2H, NH_2), 6.99 (s, 4H, H-Ar), 8.81 (s, 1H, NH) ppm; ^{13}C NMR (62.90 MHz, DMSO-d_6) δ: 21.0, 27.0, 29.4, 32.4, 37.2, 50.5, 59.4, 109.4, 122.0, 127.2, 129.0, 135.3, 144.7, 149.7, 150.5, 194.3 ppm; EIMS: m/z: 307 (M+), 292, 264, 236, 216, 160, 115, 65.

2.6.2 | 2-Amino-4-(4-hydroxyphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5c)

Yellow solid; m.p. 261–265 °C; FTIR (KBr) ν: 3517, 3432, 3328, 3226, 2962, 2177, 1666, 1651, 1623, 1606, 1483, 1375, 1269, 1169, 1046, 846, 573 cm^{-1}; ^1H NMR (250 MHz, DMSO-d_6) δ: 0.86 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.91–2.16 (dd, 2H, CH_2), 2.21–2.40 (dd, 2H, CH_2), 4.17 (s, 1H, CH), 5.63 (s, 2H, NH_2), 6.56–6.60 (d, 2H, H-Ar), 6.86–6.89 (d, 2H, H-Ar), 8.76 (s, 1H, NH), 9.09 (s, 1H, OH) ppm; ^{13}C NMR (62.90 MHz, DMSO-d_6) δ: 27.0, 29.3, 32.4, 36.6, 50.6, 59.7, 109.7, 115.1, 122.1, 128.2, 138.2, 149.4, 150.4, 155.9, 194.3 ppm; EIMS: m/z: 309 (M+), 283, 266, 252, 216, 160, 115, 105, 65.

2.6.3 | 2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5d)

Pale yellow solid; m.p. 191–195°C; FTIR (KBr) ν: 3434, 3330, 3225, 3081, 2960, 2179, 1655, 1633, 1607, 1484, 1367, 1270, 1147, 1035, 755, 564 cm^{-1}; ^1H NMR (250 MHz, DMSO-d_6) δ: 0.91 (s, 3H, CH_3), 0.99 (s, 3H,

CH_3), 1.89–2.17 (dd, 2H, CH_2), 2.26–2.46 (dd, 2H, CH_2), 4.84 (s, 1H, CH), 5.68 (s, 2H, NH_2), 7.10–7.29 (m, 4H, H-Ar), 8.89 (s, 1H, NH) ppm; ^{13}C NMR (62.90 MHz, DMSO-d_6) δ: 27.1, 29.3, 32.4, 34.6, 50.4, 58.5, 108.6, 121.3, 127.7, 127.9, 129.4, 130.1, 131.8, 145.0, 150.6, 150.7, 194.1 ppm; EIMS: m/z: 327 (M+), 292, 265, 216, 160, 132, 105, 67, 41.

2.6.4 | 2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5e)

Yellow solid; m.p. 283–286°C; FTIR (KBr) ν: 3397, 3327, 3222, 3107, 2966, 2177, 1654, 1628, 1604, 1517, 1479, 1368, 1344, 1274, 1147, 868, 566 cm^{-1}; ^1H NMR (250 MHz, DMSO-d_6) δ: 0.87 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.93–2.19 (dd, 2H, CH_2), 2.27–2.46 (dd, 2H, CH_2), 4.45 (s, 1H, CH), 5.86 (s, 2H, NH_2), 7.35–7.38 (d, 2H, H-Ar), 8.10–8.13 (d, 2H, H-Ar), 8.98 (s, 1H, NH); ^{13}C NMR (62.90 MHz, DMSO-d_6) δ: 27.1, 29.2, 32.4, 38.0, 50.3, 58.0, 108.2, 121.5, 124.0, 128.5, 146.3, 150.6, 150.9, 155.0, 194.3 ppm; EIMS: m/z: 338 (M+), 335, 306, 280, 250, 216, 179, 152, 105, 77, 41.

2.6.5 | 2-Amino-7,7-dimethyl-5-oxo-4-(pyridin-3-yl)-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (5 k)

Cream solid; m.p. 139–144°C; FTIR (KBr) ν: 3387, 3325, 3218, 2963, 2182, 1655, 1623, 1598, 1475, 1369, 1265, 1145, 1043, 837, 566 cm^{-1}; ^1H NMR (250 MHz, DMSO-d_6) δ: 0.88 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 1.95–2.44 (m, 4H, CH_2), 4.33 (s, 1H, CH), 5.83 (s, 2H, NH_2), 7.26–7.28 (d, 1H, H-Ar), 7.45–7.48 (d, 1H, H-Ar), 8.33 (s, 2H, H-Ar), 8.95 (s, 1H, NH) ppm; ^{13}C NMR (62.90 MHz, DMSO-d_6) δ: 27.0, 29.1, 32.4, 35.5, 50.3, 58.3, 108.4, 121.6, 123.9, 134.7, 142.7, 147.7, 148.7, 150.4, 150.8, 194.3 ppm; EIMS: m/z: 294 (M+), 279, 254, 237, 216, 160, 132, 117, 105, 79, 41.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the catalyst $Fe_{3\text{-}x}Ti_xO_4$@SPDETATSA

In continuation of our interest for development of more benign and efficient heterogeneous nanocatalysts and their application in organic transformations and synthesis of various heterocyclic compounds,[44,50–54] herein, we were encouraged to prepare the hitherto unreported $Fe_{3\text{-}x}Ti_xO_4$ bonded *N*-(3-silyl propyl) diethylene triamine *N,N′,N″*-tri-sulfonic acid ($Fe_{3\text{-}x}Ti_xO_4$@SPDETATSA) nanoparticles (Scheme 1), and explore their potential activity as efficient and magnetically recoverable heterogeneous catalyst for the synthesis of hexahydroquinolines (Scheme 2).

Based on the experimental results reported in the literature, the presence of Ti^{+4} cations in the structure of nanoparticles can increase the number of superficial hydroxyl groups.[55] Such a structural quality can improve the loading capacity of precursors on the surface of the $Fe_{3\text{-}x}Ti_xO_4$ MNPs. For instance, the loading amount (4.0–5.5 mmol/g) of sulfonic acid groups on the surface of the titanomagnetite nanoparticles in previously reported catalyst[44] was found to be more than the loading amounts both on magnetite Fe_3O_4 NPs (1.76 mmol/g),[56] and magnetite silica-coated Fe_3O_4 NPs (0.32 mmol/g).[57]

Following our previously reported procedure,[44] initially, the $Fe_{3\text{-}x}Ti_xO_4$ MNPs were prepared by treatment of a mixture of equimolar amounts of $FeSO_4.7H_2O$ and $TiCl_4$ in acidic solution with hydrazine monohydrate in deionized water, followed by dropwise addition of NaOH and $NaNO_3$ solution in deionised water with vigorous refluxing under nitrogen atmosphere. In the second step, the magnetically separated $Fe_{3\text{-}x}Ti_xO_4$ MNPs were modified on their external surface via one-pot reaction with 3-chloropropyltrimethoxysilane and diethylenetriamine under reflux condition. Finally, the $Fe_{3\text{-}x}Ti_xO_4$ bonded *N*-(3-silyl propyl) diethylene triamine ($Fe_{3\text{-}x}Ti_xO_4$@SPDETA) was treated with chlorosulfonic acid in CH_2Cl_2 under stirring to provide the catalyst $Fe_{3\text{-}x}Ti_xO_4$@SPDETATSA (Scheme 1).

Figure 1 shows the Fourier-transform infrared (FT-IR) spectra of the $Fe_{3\text{-}x}Ti_xO_4$, $Fe_{3\text{-}x}Ti_xO_4$@SPDETA, and $Fe_{3\text{-}x}Ti_xO_4$@SPDETATSA MNPs. The successful conjugation of *N*-(3-silyl propyl) diethylene triamine *N,N′,N″*-tri-sulfonic acid groups onto the surface of the $Fe_{3\text{-}x}Ti_xO_4$ nanoparticles was confirmed by these spectra. As shown in Figure 1a, the bands appearing at 3414 and 590 cm^{-1} were attributed to the O-H and Fe-O groups respectively.[56,58] Also, in this spectrum, symmetric stretching vibration of the Ti-O bond appears at 796 cm^{-1}.[59,60] In the IR spectrum of the $Fe_{3\text{-}x}Ti_xO_4$@SPDETA MNPs (Figure 1b), in addition to the bands shown in Figure 1a, extra bands assigned to the CH_2 groups at 2922[59,60] and 1463 cm^{-1},[49] Si-C bonds at 1110 cm^{-1}[45] and Si-O bonds at 1030 cm^{-1}[49,58,60] are observed. In addition, the IR spectrum of the $Fe_{3\text{-}x}Ti_xO_4$ @SPDETATSA MNPs (Figure 1c) exhibits the bands at 988 and 1203 cm^{-1} attributed to S-O and S=O bonds respectively.[56,57] Broadening of the bands shown at 3000–3500 cm^{-1} for the sulfonic acid hydroxyl group[58] confirms the successful attachment of the sulfonic acid groups onto the $Fe_{3\text{-}x}Ti_xO_4$@SPDETA MNPs.

As shown in Figure 2, the elemental composition of the $Fe_{3\text{-}x}Ti_xO_4$@SPDETATSA MNPs was identified by energy-dispersive X-ray spectroscopy (EDX). As shown in this figure, EDX pattern obviously approves the composition of the $Fe_{3\text{-}x}Ti_xO_4$@SPDETATSA nanoparticles. It has been

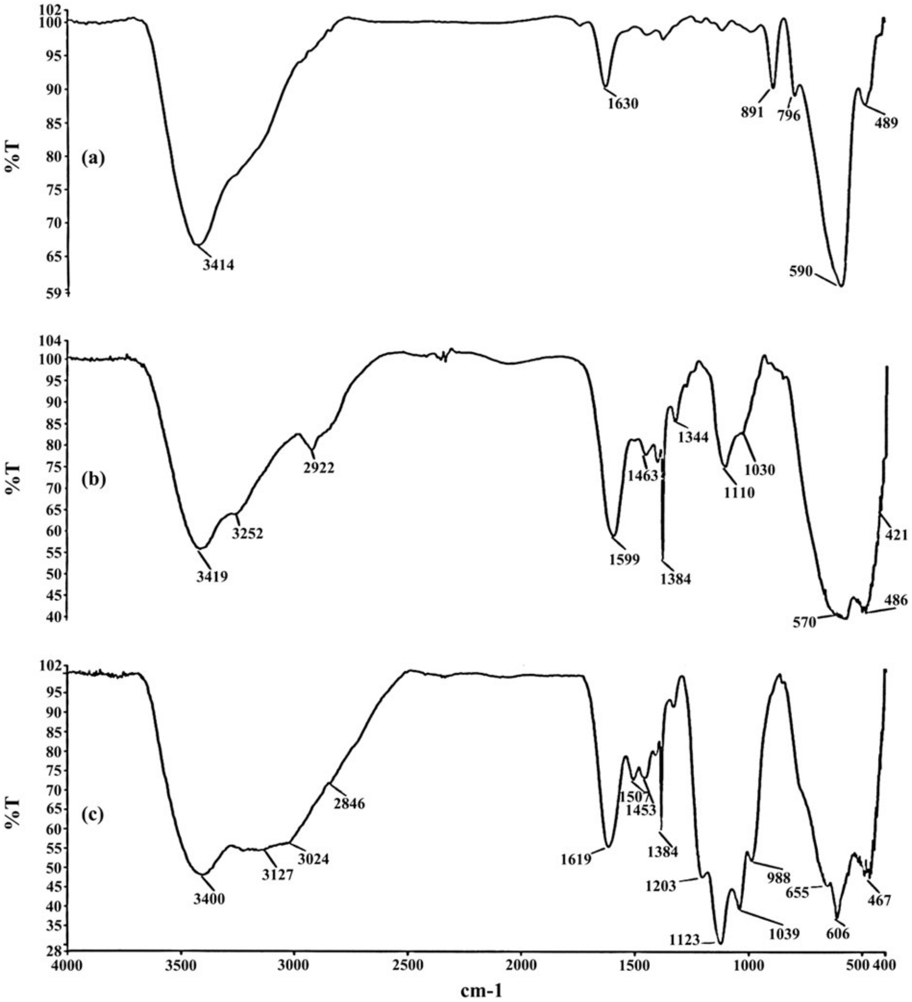


FIGURE 1 FT-IR spectra of: (a) $Fe_{3-x}Ti_xO_4$ MNPs, (b) $Fe_{3-x}Ti_xO_4$@SPDETA MNPs and (c) $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs

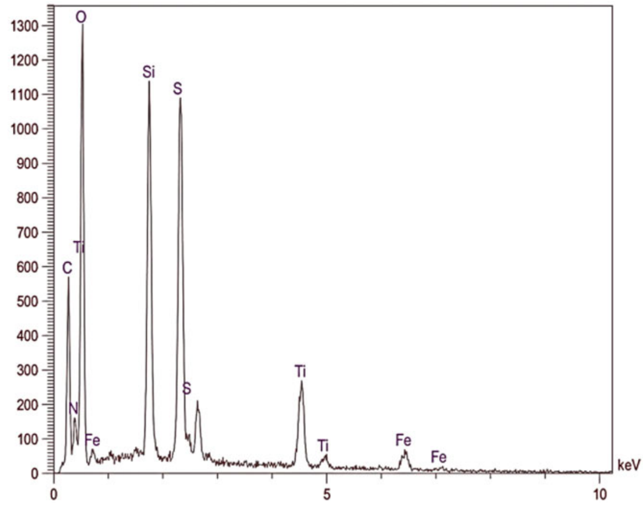


FIGURE 2 EDX pattern of the $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs

indicated by chemical characterization of the typical sample that the $Fe_{3-x}Ti_xO_4$@SPDETATSA is composed of Fe (1.83%), Ti (4.54%), Si (5.73%), C (25.46%), O (39.55%), N (13.45%) and S (7.92%) elements.

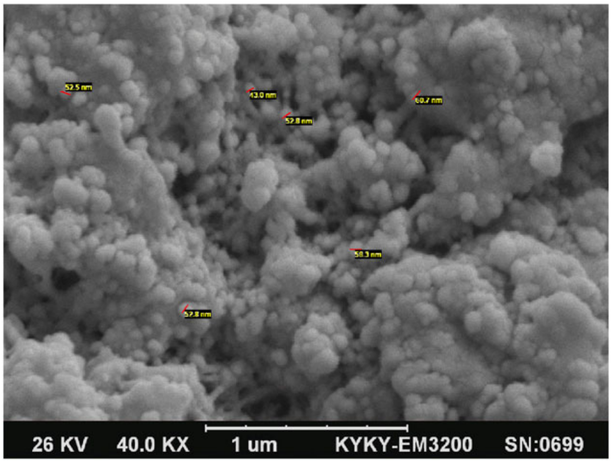


FIGURE 3 Scanning electron microscopy (SEM) image of $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs

The SEM and TEM images of $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs are shown in Figure 3 and 4. Based on these images, it is confirmed that the $Fe_{3-x}Ti_xO_4$@SPDETATSA catalyst is made up of nanometre-sized particles. Figures 3 and 4

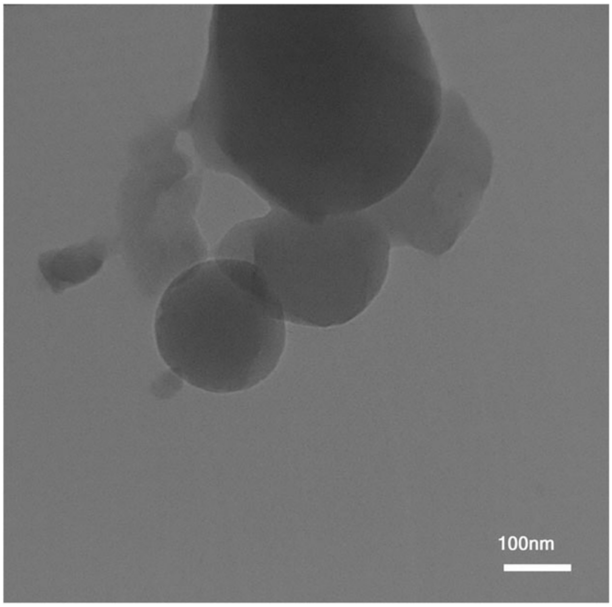


FIGURE 4 Transmission electron microscopy (TEM) image of $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs

show that the $Fe_{3-x}Ti_xO_4$@SPDETATSA nanoparticles have spherical structure.

The magnetic property of $Fe_{3-x}Ti_xO_4$ and $Fe_{3-x}Ti_xO_4$ @SPDETATSA nanoparticles was characterized by using a vibrating sample magnetometer (VSM) at 300 K. As shown in Figure **5**, the magnetization curves measured for $Fe_{3-x}Ti_xO_4$ and $Fe_{3-x}Ti_xO_4$@SPDETATSA nanoparticles are compared. As seen in Figure 5, the values of the saturation magnetization are 33.854 and 6.265 emu/g for $Fe_{3-x}Ti_xO_4$ and $Fe_{3-x}Ti_xO_4$@SPDETATSA nanoparticles respectively in +10000 Oe. The reduction in the saturation magnetization proposes the successful formation of $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs. Despite such a decrement in the saturation magnetization, the catalyst can still be efficiently separated from the solution simply by using an external magnet.

As illustrated in Figure 6, decomposition profile of the prepared $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs was monitored by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA). The weight loss exhibited in the range 25–153°C (centred at 100°C) can be assigned to desorption of water or other organic solvents used during the preparation of the catalyst. Also, as the TGA thermogram exhibits, a significant decrement in the weight percentage of the $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs as shown in the range 153–324°C and centred at 240°C is likely attributed to the loss of the immobilized sulfonic acid groups. Further increasing the temperature to 500°C (centred at about 430°C) brought about a significant loss of weight likely due to the complete removal of the organic spacer group. Accordingly, as shown in Figure **6**, the differential thermal analysis (DTA) was performed on this catalyst which exhibits three major bands centred at about 100, 240 and 430°C corresponding to the aforementioned major decomposition steps.

3.2 | Catalytic activity of $Fe_{3-x}Ti_xO_4$@SPDETATSA for the synthesis of hexahydroquinoline derivatives

In order to establish the reaction conditions for the synthesis of hexahydroquinolines, the reaction between benzaldehyde, dimedone, malononitrile, and ammonium acetate in the presence of the catalyst was chosen as the model reaction and the effects of reaction parameters on this reaction were studied (Table 1). The experimental results summarized in Table 1, clearly indicate the effective catalytic performance of the $Fe_{3-x}Ti_xO_4$@SPDETATSA nanoparticles for this reaction. The optimal catalyst loading and temperature of the reaction were found to be 0.04 g

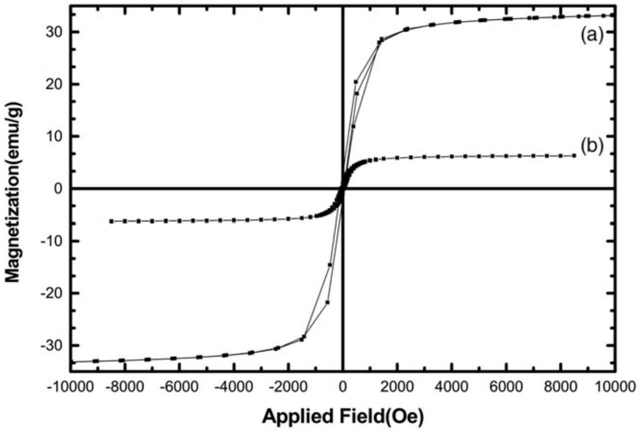


FIGURE 5 VSM patterns of (a) $Fe_{3-x}Ti_xO_4$ and (b) $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs

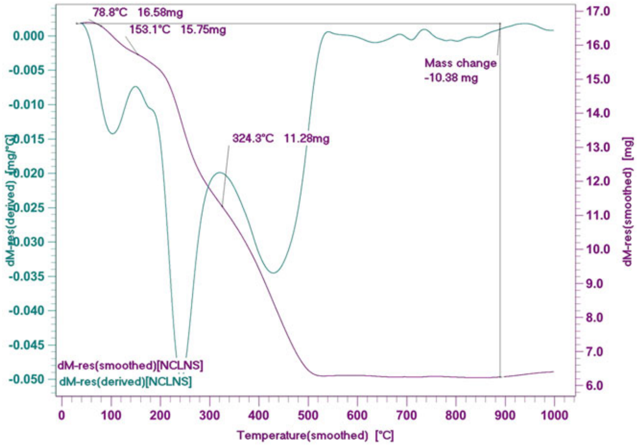
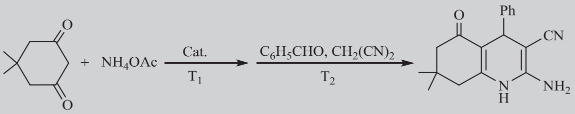


FIGURE 6 TGA and DTA curves of the $Fe_{3-x}Ti_xO_4$@SPDETATSA nanocatalyst

TABLE 1 Screening the reaction parameters on the synthesis of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile[a]



Entry	Catalyst (g)	Temperature (°C)	T_1(min)	T_2(min)	Yield (%)[b]
1	0.02	75	50	40	80
2	0.03	75	45	30	88
3	0.04	75	40	20	91
4	0.05	75	40	20	90
5	0.00	75	100	60	37
6	0.04	80	35	20	89
7	0.04	90	30	20	86
8	0.04	60	90	60	52
9	0.04	r.t.	120	70	43

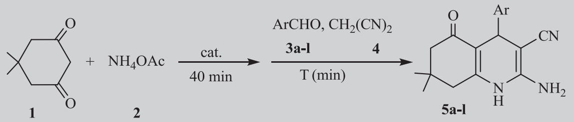
[a] Conditions: dimedone (1 mmol), ammonium acetate (1.5 mmol) benzaldehyde (1 mmol), malonontrile (1 mmol).

[b] Isolated pure yield.

per mmol of aldehyde and 75°C respectively (entry 3). No improvement of the reaction yield was observed upon increasing the amount of the catalyst (entry 4). The importance of the catalyst in the reaction was verified by conducting the reaction in the absence of the catalyst that resulted in low reaction yield after a prolonged reaction time (entry 5).

To establish the generality of the reaction, a diverse series of aromatic aldehydes **3a–l** were subjected to this reaction under the optimized conditions (Scheme 2). The results are summarized in Table 2. In general, the reactions proceeded very fast and smoothly to furnish the products **5a–l** in excellent and comparable yields irrespective of the nature of the aromatic rings. All the obtained products are known

TABLE 2 Synthesis of hexahydroquinolines catalyzed by $Fe_{3\text{-}x}Ti_xO_4$@SPDETATSA MNPs[a]



Entry	Ar	Product	T (min)[b]	Yield (%)[c]	Mp (°C)	
					Found	Reported
1	C_6H_5	**5a**	20	91	277–280	276–278[45]
2	4-MeC_6H_4	**5b**	20	84	291–294	294–295[46]
3	4-OHC_6H_4	**5c**	25	78	261–265	268–270[45]
4	2-ClC_6H_4	**5d**	10	90	191–195	211–213[47]
5	4-$NO_2C_6H_4$	**5e**	15	93	283–286	286–288[45]
6	3-$NO_2C_6H_4$	**5f**	10	87	280–284	282–283[48]
7	3-OHC_6H_4	**5 g**	25	89	280–283	284–286[45]
8	4-$OMeC_6H_4$	**5 h**	20	90	285–288	285–287[36]
9	2,4-$Cl_2C_6H_3$	**5i**	15	84	185–190	190–192[47]
10	4-FC_6H_4	**5j**	15	92	268–274	270–272[45]
11	3-C_5H_4N	**5 k**	25	85	139–144	–
12	2-C_4H_3S	**5 l**	25	83	257–261	256–257[49]

[a] Conditions: dimedone (1 mmol), ammonium acetate (1.5 mmol) benzaldehyde (1 mmol), malonontrile (1 mmol), catalyst (0.04 g), 75°C.

[b] T refers to the second step reaction time. The first step reaction time is 40 min for all the reactions.

[c] Isolated pure yield.

compounds which are characterized on the basis of their physical and spectral (FT-IR, ^{1}H NMR, ^{13}C NMR and mass) analysis and compared with the corresponding reported data (Table 2).

3.3 | Catalytic reaction mechanism

A plausible mechanism proposed to explain the formation of hexahydroquinolines is depicted in Scheme 3. In the first step, the catalyst-promoted amination of dimedone occurs to produce the 3-amino-5,5-dimethylcyclohex-2-enone intermediate **I**. On the other hand, the catalyst-activated Knoevenagel condensation reaction between malononirile and the aldehyde takes place to produce the intermediate **II**. In the following step, the nucleophilic addition reaction between the intermediates **I** and **II** takes place to yield the adduct **A** which undergoes intramolecular nucleophilic cyclization to afford the products **5a–l**.

3.4 | Reusability of the catalyst

The possible recyclability of the catalyst $Fe_{3-x}Ti_xO_4$ @SPDETATSA was examined for the aforementioned model reaction for the synthesis of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5a**) under the optimized conditions. After completion of the reaction, the catalyst was isolated from the reaction mixture simply by employing a magnet. The recovered catalyst was washed with ethanol, dried in oven at 76 °C for 1 h. As shown in Figure 7, the recycled catalyst could be reused for four fresh runs without any appreciable loss of the catalytic activity.

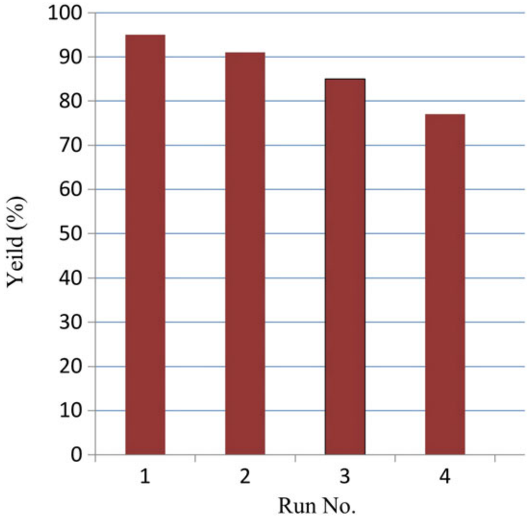
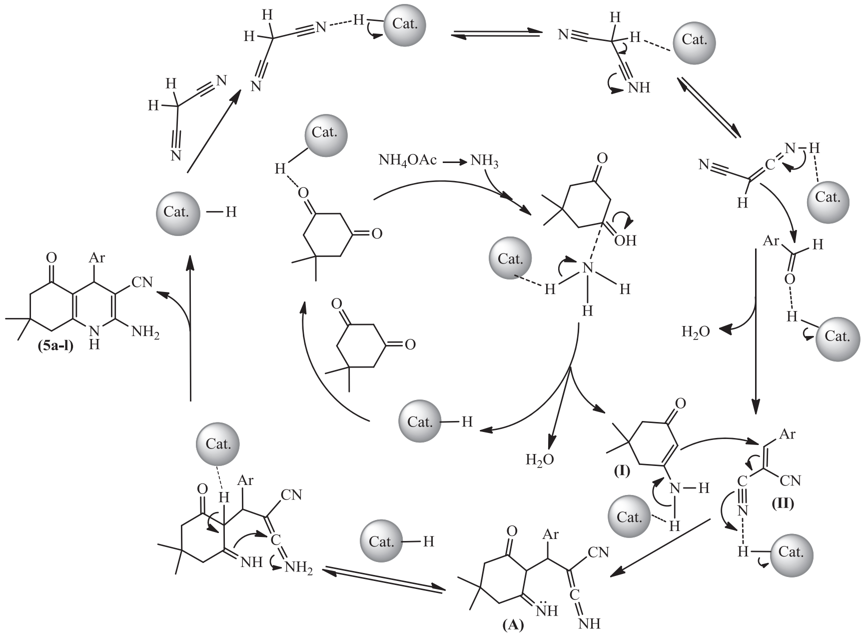


FIGURE 7 Recyclability of the catalyst ($Fe_{3-x}Ti_xO_4$@SPDETATSA) in the synthesis of **5a** under the optimized condition

4 | CONCLUSION

In summary, we have synthesized $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs as a novel, effective and magnetically recyclable acidic nano catalyst and characterized by different analytical techniques as described. In continuation, the catalytic activity of the prepared nanoparticles was explored in one-pot tandem reaction between dimedone, ammonium acetate, aldehyde and malononitrile to produce hexahydroquinoline derivatives. The reactions proceed smoothly under green conditions to yield the respective products in excellent yields and reasonably short reaction times. It is expected that, this catalyst



SCHEME 3 The proposed mechanism for the synthesis of hexahydroquinolines catalyzed by $Fe_{3-x}Ti_xO_4$@SPDETATSA MNPs

could be employed as a versatile acid catalyst in the synthesis of other heterocyclic compounds and various other organic transformations.

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