

Fe₃O₄@SiO₂@Propyl-ANDSA: A New Catalyst for the Synthesis of Substituted Pyrroles

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Substituted pyrroles are an essential class of heterocyclic compounds. In this research, an efficient and eco-friendly method has been developed for the synthesis of pyrrole derivatives from the reaction of 2,5-hexanedione and primary amines. Magnetic nanoparticles supported on functionalized 7-aminonaphthalene-1,3-disulfonic acid-functionalized silica (Fe₃O₄@SiO₂@Propyl-ANDSA) has been investigated as a novel catalyst in this reaction. Herein, a novel catalyst was developed for an efficient and environmentally friendly synthesis of pyrrole in excellent yields. It should also be noted that Fe₃O₄@SiO₂@Propyl-ANDSA as a reaction catalyst could be recovered quickly and reused for several times without any decrease in efficiency. With its operational simplicity, green nature, and high yields the reaction will be acting as an appropriate alternative for the synthesis of substituted pyrroles.

Keywords: Fe₃O₄@SiO₂@Propyl-ANDSA, Heterocyclic compounds, Pyrroles, Functionalized silica

INTRODUCTION

Heterocyclic compounds containing pyrrole ring, as a kernel unit, are important targets which are known to display several biological activities [1]. Pyrrole is known to be a part of certain drugs such as Atorvastatin [2], Pyrvinium [3] and Zomepirac [4]. For example, Zomepirac is an orally effective non-steroidal anti-inflammatory drug (NSAID) that has antipyretic actions [4]. Pyrvinium salts can inhibit the growth of cancer cells [3] and Atorvastatin is a member of the drug class known as statins which are used primarily as a lipid-lowering agent for prevention of events associated with cardiovascular disease [2] (Fig. 1). One of the most common strategies for the pyrrole synthesis is the Paal-Knorr reaction in which 1,4-dicarbonyl compounds in reaction with an excess of a primary amine or ammonia are converted to pyrroles. Many catalysts have been used for this conversion, such as Bi(NO₃)₃·5H₂O [5], Sc(OTf)₃ [6], ruthenium [7], TiCl₄/Et₃N [8] Fe₃O₄@PEG400-SO₃H [9], CAN [10], enzyme-catalyzed [11] and

silica sulfuric acid [12].

Although these reported protocols find certain merits of their own, unfortunately some of these procedures require the expensive or toxic catalysts, high reaction temperatures, and long reaction times or lead to low yields. Therefore, application of a milder, selective, safe, and recyclable catalyst is still in demand.

One of the interesting properties of nano-materials is that they have a high specific surface area of the active part, leading to an additional exposed area. [13] Moreover, a higher surface area gives the nanomaterials a more active surface; they are not easily separated. Therefore, it is attractive to design a recoverable and well-dispersed catalyst.

Magnetite nanoparticles (MNPs) as catalysts are very promising because of their magnetic properties and large specific surface area [14-15]. In continuation of our studies in the synthesis of various heterocyclic compounds [16], and since Fe₃O₄@SiO₂@Propyl-ANDSA was proved to be an efficient heterogeneous nano magnetic acid catalyst in multicomponent reactions [17], in this study, we would like to explore the application of this novel catalyst in the

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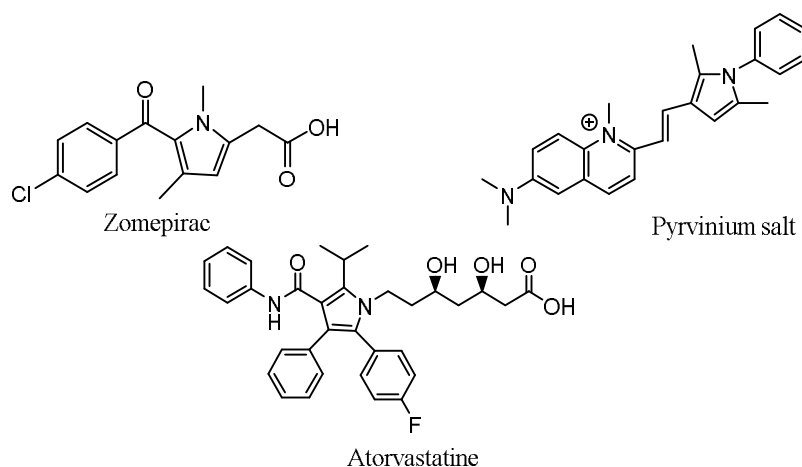
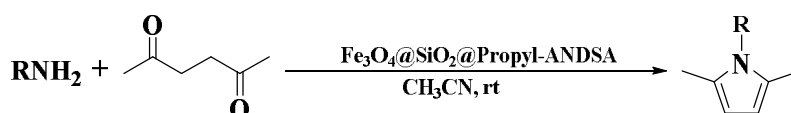


Fig. 1. The structure of some biologically active pyrrole derivatives.



Scheme 1. One-pot synthesis of pyrrole derivatives

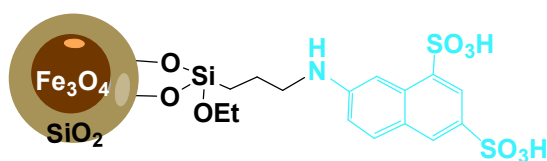


Fig. 2. The structure of Fe₃O₄@SiO₂@Propyl-ANDSA.

synthesis of pyrrole derivatives. Herein, an efficient procedure has been described for the synthesis of pyrrole derivatives in excellent yields from the reaction of 1,4-dicarbonyl compounds and primary amines at room temperature (Scheme 1). Magnetic nanoparticles supported with functionalized 7-aminonaphthalene-1,3-disulfonic acid-functionalized silica (Fe₃O₄@SiO₂@Propyl-ANDSA) have been evaluated as the catalyst in this reaction (Fig. 2).

EXPERIMENTAL

Materials and Instrumentation

All commercially available chemicals were purchased from Merck and Fluka companies. Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ on

Bruker Avance spectrometers of 90 MHz for ¹H NMR and 62.5 MHz for ¹³C NMR using TMS as an internal standard; chemical shifts were expressed in parts per million (ppm). Infrared (IR) spectroscopy was recorded on a Perkin Elmer GX FT-IR spectrometer. Mass spectra were recorded on a Shimadzu QP 1100 BX Mass Spectrometer. Melting points were determined on Stuart Scientific SMP3 apparatus.

Scanning electron microscopy (SEM) was performed on EM3200 instrument operated at 30 kV accelerating voltage. The qualitative analysis of Fe₃O₄@SiO₂@Propyl-ANDSA was performed by using energy-dispersive X-ray spectroscopy (EDX). Energy dispersive X-ray analysis of the prepared catalyst was performed on a FESEM-SIGM (Germany) instrument. Thermo-gravimetric analysis (TGA) was performed on a PYRIS DIAMOND. To measure the

magnetic attributes of the sample, a vibrating sample magnetometer (VSM) instrument MDKFT was utilized. Ultrasonication was done in a 2200 ETH-SONICA ultrasound cleaner with a frequency of 45 kHz.

General Procedure

A mixture of substituted anilines (1 mmol), 2,5-hexadione (1 mmol) and Fe₃O₄@SiO₂@Propyl-ANDSA (0.05 g) was stirred at room temperature for appropriate times, as shown in Table 1. The progress of the reaction was monitored by TLC (10:3, *n*-hexane/acetone). After completion of the reaction, the reaction mixture was dissolved in acetonitrile, and the nano-catalyst was separated by using an external magnet. Evaporation of the solvent under reduced pressure resulted in the final products, and for further purification, EtOH 95% (5 ml) was added. The precipitate was then filtered off and washed with cold ethanol. After drying, the pure product was obtained and characterized *via* different techniques.

Selected Spectral Data of Substituted Pyrroles Derivatives (Table 2)

Compound 3-(2-(2,5-dimethyl-1H-pyrrol-1-yl) ethyl-1H-indole (3f). (brown solid, m.p.: 175-176 °C). IR (nujol): ν_{\max} 3250, 3020, 1605, 1520, 1499, 1455, 1370, 1016 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz) δ 2.24 (s, CH₃, 6H), 3.06 (t, *J* = 15.5 Hz, CH₂, 2H), 4.04 (t, *J* = 15.5 Hz, CH₂, 2H), 5.83 (s, pyrrolics, 2H), 6.87 (s, CH, 1H), 7.12-7.73 (m, PhH, 4H), 7.94 ppm (s, NH, 1H). Found: M⁺ 238.1524. C₁₆H₁₈N₂ requires M, 238.1536. Anal. Calcd. For C₁₆H₁₈N₂: C, 75.00; H, 7.03; N, 10.93. Found: C, 74.49; H, 6.98; N, 10.39.

Compound 1,4-bis((2,5-dimethyl-1H-pyrrol-1-yl) methyl benzene (3h). (cream solid, m.p.: 197-198 °C). IR (KBr): ν_{\max} 1515, 1462, 1410, 1377, 1303, 1019 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ 2.13 (s, CH₃, 12H), 4.97 (s, CH₂, 4H), 5.84 (s, pyrrolics, 4H), 6.82 ppm (s, PhH, 4H). Found: M⁺ 292.1939. C₂₀H₂₄N₂ requires M, 292.1946. Anal. Calcd. for C₂₀H₂₄N₂: C, 78.29; H, 8.54; N, 9.96. Found: C, 79.88; H, 8.16; N, 8.97.

Compound 4-(2,5-dimethyl-1H-pyrrol-1-yl) benzoic acid (3i). (pale yellow solid, m.p.: 174-175 °C). IR (nujol): ν_{\max} 2400, 2200, 1678, 1607, 1463, 1377, 1324, 1129, 1106 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ 2.00 (s, CH₃, 6H), 5.90 (s, pyrrolics, 2H), 7.30 (d, *J* = 10.1 Hz, PhH, 2H), 8.20 (d,

J = 10.1 Hz, PhH, 2H), 11.39 ppm (b, COOH, 1H). Found: M⁺ 215.0946. C₁₃H₁₃NO₂ requires M, 215.1125. Anal. Calcd. for C₁₃H₁₃NO₂: C, 72.55; H, 6.04; N, 6.51. Found: C, 71.84; H, 6.00; N, 6.22.

Compound 1,4-bis(2,5-dimethyl-1H-pyrrol-1-yl) benzene (3j). (pale yellow solid, m.p.: 256-257 °C). IR (KBr): ν_{\max} 1514, 1463, 1378, 1310, 1211, 1001 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ 2.10 (s, CH₃, 12H), 5.90 (s, pyrrolics, 4H), 7.25 ppm (s, PhH, 4H). Found: M⁺ 264.1626. C₁₈H₂₀N₂ requires M, 264.1632. Anal. Calcd. for C₁₈H₂₀N₂: C, 76.59; H, 7.09; N, 9.92. Found: C, 77.37; H, 6.99; N, 9.61.

Compound 1,3-bis(2,5-dimethyl-1H-pyrrol-1-yl) benzene (3k). (brown solid, m.p.: 99-100 °C). IR (nujol): ν_{\max} 1600, 1521, 1499, 1459, 1377, 1321, 1006 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz): δ 2.10 (s, CH₃, 12H), 5.94 (s, pyrrolics, 4H), 7.12-7.68 ppm (m, PhH, 4H). Found: M⁺ 264.1626. C₁₈H₂₀N₂ requires M, 264.1637. Anal. Calcd. for C₁₈H₂₀N₂: C, 79.12; H, 7.32; N, 10.25. Found: C, 79.46; H, 7.62; N, 10.75.

Compound bis(2-(2,5-dimethyl-1H-pyrrol-1-yl)ethyl amine (3l). (yellow solid, m.p.: 74-75 °C). IR (nujol): ν_{\max} 3312, 2915, 2854, 1663, 1571, 1517, 1463, 1404, 1377, 1298, 1121, 1108 cm⁻¹. ¹H NMR (CDCl₃, 250 MHz), δ 2.30 (s, CH₃, 12H), 2.70 (t, *J* = 17.91 Hz, CH₂, 4H), 3.75 (t, *J* = 18.5 Hz, CH₂, 4H), 5.70 ppm (s, pyrrolics, 4H). Found: M⁺ 259.2048. C₁₆H₂₅N₃ requires M, 259.2055. Anal. Calcd. for C₁₆H₂₅N₃: C, 74.13; H, 9.65; N, 16.21. Found: C, 73.48; H, 9.88; N, 16.07

Compound tris(2-(2,5-dimethyl-1H-pyrrol-1-yl)ethyl amine (3m). (pale yellow solid, m.p.: 110-111 °C). IR (nujol): ν_{\max} 3100, 2854, 2739, 1571, 1518, 1464, 1407, 1378, 1298, 1166, 1061, 1016, 745 cm⁻¹. ¹H NMR (CDCl₃, 90 MHz) 2.25 (s, CH₃, 18H), 2.74 (t, *J* = 19.7 Hz, CH₂, 6H), 3.75 (t, *J* = 19.7 Hz, CH₂, 6H), 5.78 ppm (s, pyrrolics, 6H). Found: M⁺ 380.3021. C₂₄H₃₆N₄ requires M, 380.3044. Anal. Calcd. for C₂₄H₃₆N₄: C, 74.04; H, 9.51; N, 14.39. Found: C, 74.11; H, 9.67; N, 14.79.

RESULTS AND DISCUSSION

Magnetically recyclable core/shell nanocomposite was synthesized through different methods [18]. For example, MNPs@SiO₂ was synthesized through the modified method

Table 1. Optimizing the Reaction Conditions for the Synthesis of 3b Using Fe₃O₄@SiO₂@Propyl-ANDSA as the Catalyst

Entry	Catalyst	Temp. (°C)	Solvent	Time (min)	Yield (%) ^a
1	-	100 °C	Solvent-free	6	- ^b
2	MNPs@SiO ₂ -Pr-ANDSA (0.02 g) ^c	r.t.	Solvent-free	20	79
3	MNPs@SiO ₂ -Pr-ANDSA (0.03 g) ^c	r.t.	Solvent-free	15	83
4	MNPs@SiO ₂ -Pr-ANDSA (0.04 g) ^c	r.t.	Solvent-free	10	90
5	MNPs@SiO ₂ -Pr-ANDSA (0.05 g) ^c	r.t.	Solvent-free	15	93
6	MNPs@SiO ₂ -Pr-ANDSA (0.06 g) ^c	r.t.	MeCN	10	93
7	MNPs@SiO ₂ -Pr-ANDSA (0.07 g) ^c	r.t.	MeCN	10	89
8	MNPs@SiO ₂ -Pr-ANDSA (0.05 g) ^c	40 °C	MeCN	10	93
9	MNPs@SiO ₂ -Pr-ANDSA (0.05 g) ^c	50 °C	MeCN	10	91
10	MNPs@SiO ₂ -Pr-ANDSA (0.05 g)	50 °C	H ₂ O/EtOH	20	75
11	MNPs@SiO ₂ -Pr-ANDSA (0.05 g)	50 °C	H ₂ O	25	70
12	MNPs@SiO ₂ -Pr-ANDSA (0.05 g)	50 °C	EtOH	20	80
13	MNPs@SiO ₂ -Pr-ANDSA (0.05 g)	50 °C	MeCN	15	80
14	MNPs@SiO ₂ (0.2 g)	r.t.	MeCN	60	75

^aIsolated yield. ^bNo reaction occurred under solvent-free condition at room temperature. ^cReaction condition: 1,4-dicarbonyl (1 mmol), aniline (1 mmol), solvent-free conditions.

of Stöber [19], and then, it was functionalized with 7-aminonaphthalene-1,3-disulfonic to obtain Fe₃O₄@SiO₂@Propyl-ANDSA.

Preparation of 7-Aminonaphthalene-1,3-disulfonic acid-functionalized Magnetic Fe₃O₄ Nanoparticles (Fe₃O₄@SiO₂@Propyl-ANDSA)

There are four major steps for the synthesis procedure of the magnetic Fe₃O₄@SiO₂@Propyl-ANDSA. Firstly, naked magnetic Fe₃O₄ nanoparticles were prepared through coprecipitation of iron(II) and iron(III) ions. Secondly, the magnetic NPs were coated with a silica shell by using tetraethylorthosilicate (TEOS) [19]. Thirdly, the Fe₃O₄@SiO₂ nanoparticles

were coated by (3-chloropropyl)-triethoxysilane, yielding the chloro functionalized nanoparticles (Fe₃O₄@SiO₂@Cl MNPs) [20]. Finally, the Fe₃O₄@SiO₂@Cl nanoparticles reacted with 7-aminonaphthalene-1,3-disulfonic acid to yield Fe₃O₄@SiO₂@Propyl-ANDSA. The acidic content of Fe₃O₄@SiO₂@Propyl-ANDSA was characterized by determination of H⁺ of the catalyst through back titration with NaOH (0.1 M) (Scheme 2).

The effect of Fe₃O₄@SiO₂@Propyl-ANDSA as the catalyst was examined in the synthesis of the model compound 2,5-dimethyl-1-phenyl-1*H*-pyrrole 3b from the reaction of 2,5-hexanedione and aniline.

First, the reaction progress was examined in the absence

Table 2. Synthesis of Substituted Pyrroles Using Fe₃O₄@SiO₂@Propyl-ANDSA as the Catalyst at Room Temperature^a

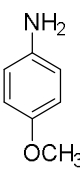
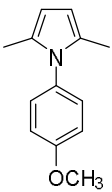
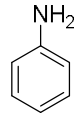
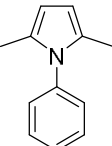
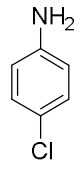
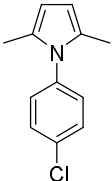
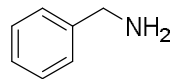
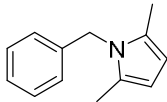
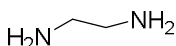
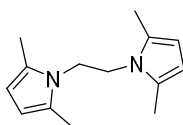
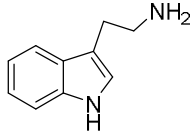
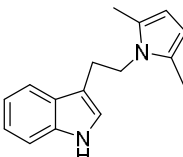
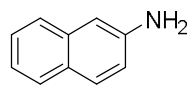
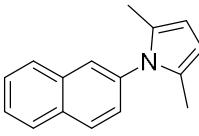
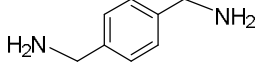
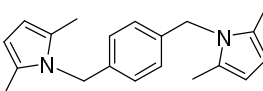
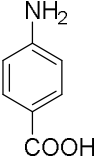
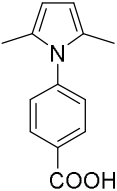
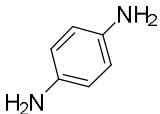
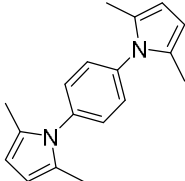
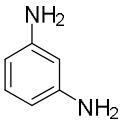
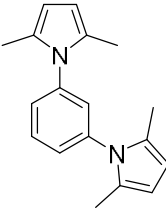
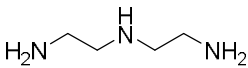
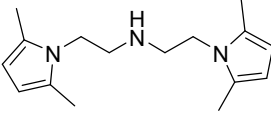
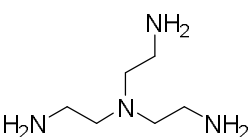
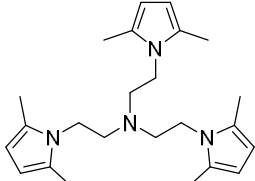
Comp.	Amine	Product	Time (min)	Yield (%) ^b
3a			10	96
3b			10	93
3c			15	82
3d			5	90
3e			10	90
3f			20	88
3g			20	70
3h			15	86

Table 2. Continued

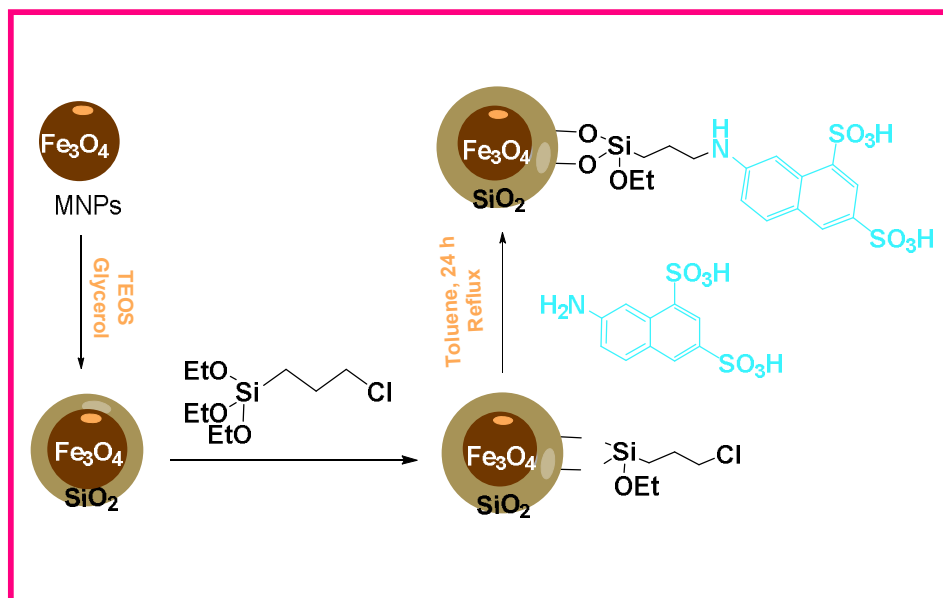
3i			35	74
3j			30	93
3k			20	90
3l			5	85
3m			15	80

^aReaction condition: 1,4-dicarbonyl compound (1 mmol) and aniline (1 mmol) at room temperature.

^bIsolated yield.

of a catalyst and it was observed that the reaction could not proceed without the catalyst even after a prolonged reaction time under solvent-free condition at room temperature (Table 1, entry 1). The same model reaction was carried out in the presence of different amounts of the catalyst under solvent-free conditions at room temperature (Table 1, entries 2-5). It was determined that 0.05 g of catalyst is optimal to this reaction (Table 1, entry 5) and the yield of

product did not increase. With increasing the catalyst to more than 0.05 g (Table 1, entries 6-7). Furthermore, different temperatures were tested in this reaction (Table 1, entries 8-9) and it was found that room temperature is the best temperature for this reaction (Table 1, entry 5). The application of this catalyst was also investigated in the presence of different solvents including EtOH, H₂O/EtOH (1:1), and MeCN (Table 1, entries 10-13). Also, the effect



Scheme 2. The synthetic pathway of Fe₃O₄@SiO₂@Propyl-ANDSA

Table 3. Comparison of Different Methods in the Synthesis of 1-(4-Methoxyphenyl)-2,5-dimethyl-1H-pyrrole 3a

Entry	Catalyst	Solvent/Temperature	Time	Yield (%) ^a	Ref.
1	Fe ₃ O ₄ @SiO ₂ @Propyl-ANDSA	CH ₃ CN, r.t.	10 min	96	This work
2	Fe ₃ O ₄ @PEG400-SO ₃ H	Solvent-free, r.t.	20 min	92	[9]
3	CAN	MeOH, r.t.	30 min	88	[10]
4	Enzyme-catalyzed	CH ₃ OH, 50 °C	5 h	97	[11]
5	Silica Sulfuric Acid	Solvent-free, r.t.	10 min	95	[12]

of H₂O was investigated in this reaction. It was concluded that in the presence of water the reaction was less progressed compared with other solvents (Table 1, entry 11). The results showed that acetonitrile is the most efficient solvent in comparison with other solvents. According to the obtained results, subsequent studies were carried out under the following optimized conditions, that is, in the presence of Fe₃O₄@SiO₂@Propyl-ANDSA (0.05 g) at room

temperature, in acetonitrile as the solvent (Table 1, entry 13). Also, the reaction in the presence of MNPs@SiO₂ was less progressed compared with MNPs@SiO₂-Pr-ANDSA (Table 1, entry 14)

Then, to evaluate the generality and versatility of this methodology, various aromatic anilines were used under optimized conditions. As shown in Table 2, both electron-rich and electron-deficient anilines gave pyrrole derivatives in good

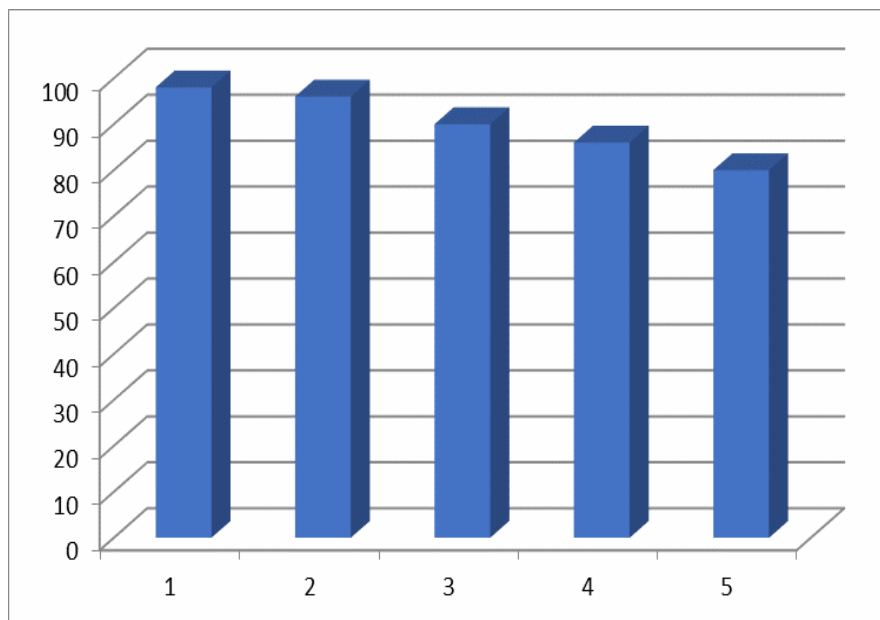
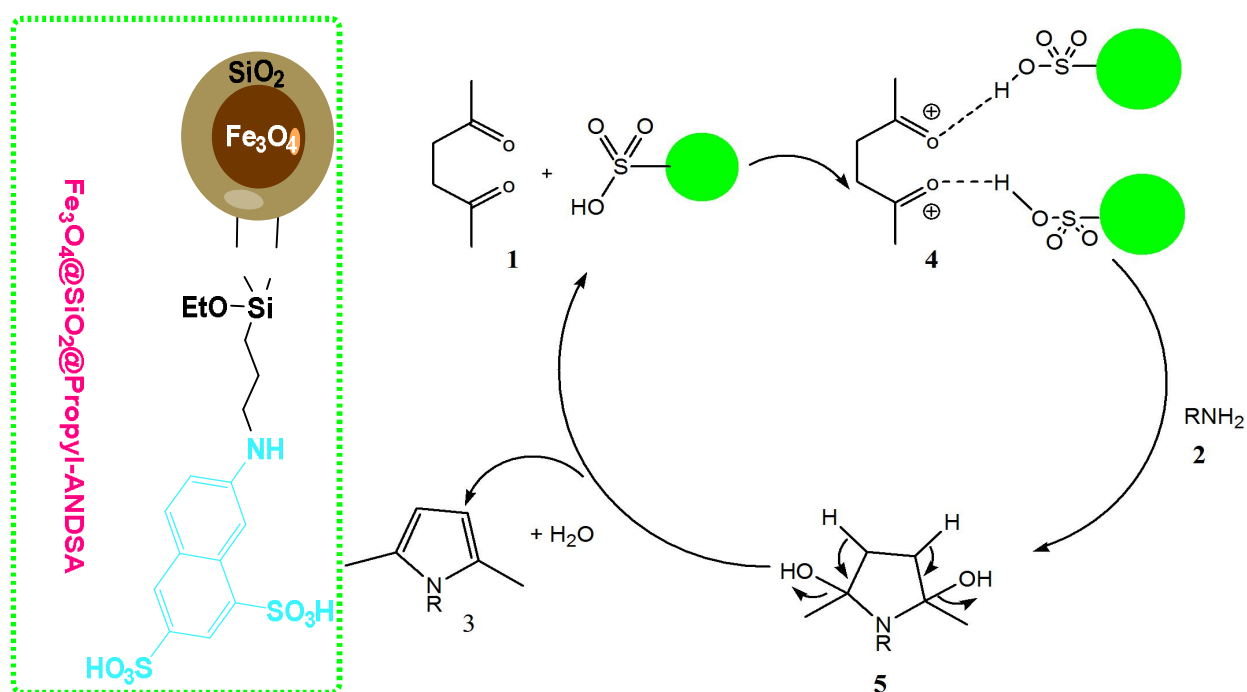


Fig. 3. Recyclability test of Fe₃O₄@SiO₂@Propyl-ANDSA.



Scheme 3. Suggested mechanism for the synthesis of pyrrole derivatives in the presence of Fe₃O₄@SiO₂@Propyl-ANDSA.

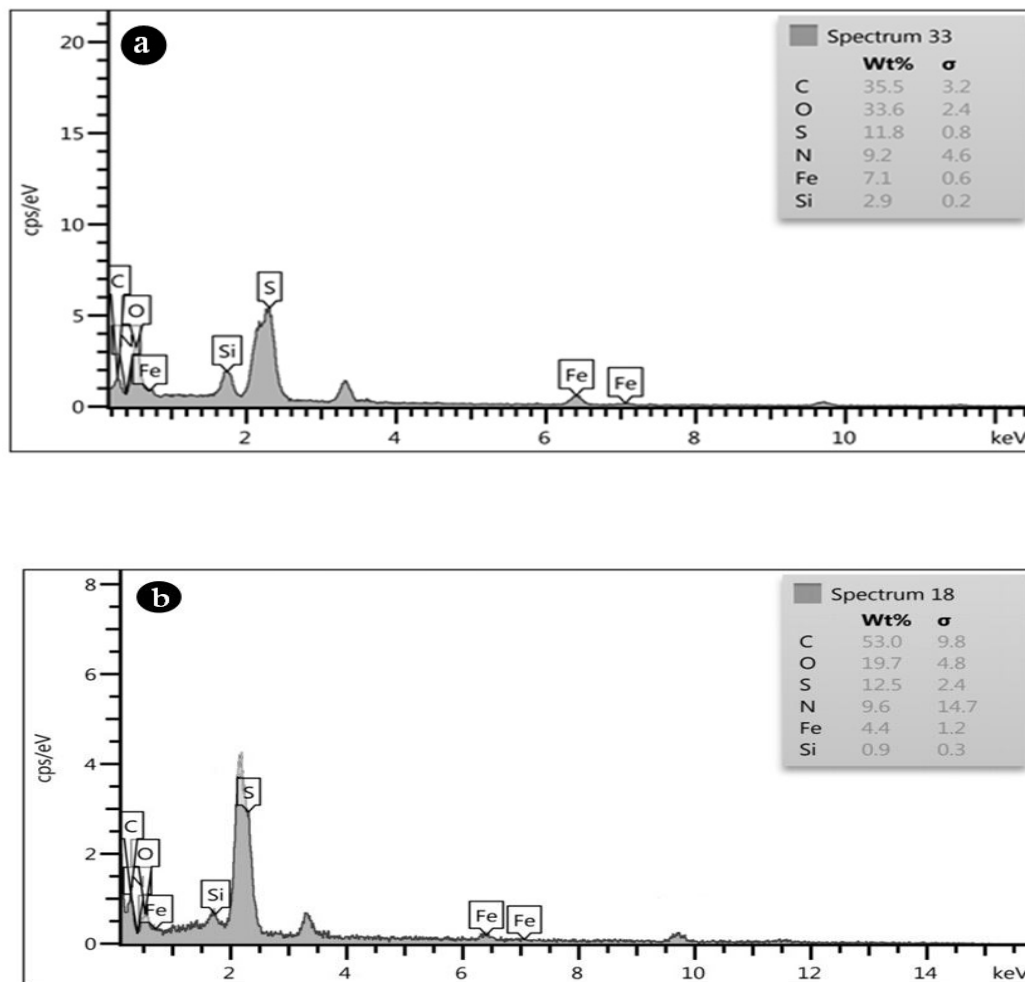


Fig. 4. EDX spectra of Fe₃O₄@SiO₂@Propyl-ANDSA before (a) and after (b) the reaction.

Table 4. CHNS Analysis of Fe₃O₄@SiO₂@Propyl-ANDSA

CHNS analysis of Fe ₃ O ₄ @SiO ₂ @Propyl-ANDSA				
Element	C	H	N	S
Percent (%) (before catalytic reaction)	24.04	4.50	5.74	12.96
Percent (%) (after catalytic reaction)	24.05	4.52	5.73	12.95

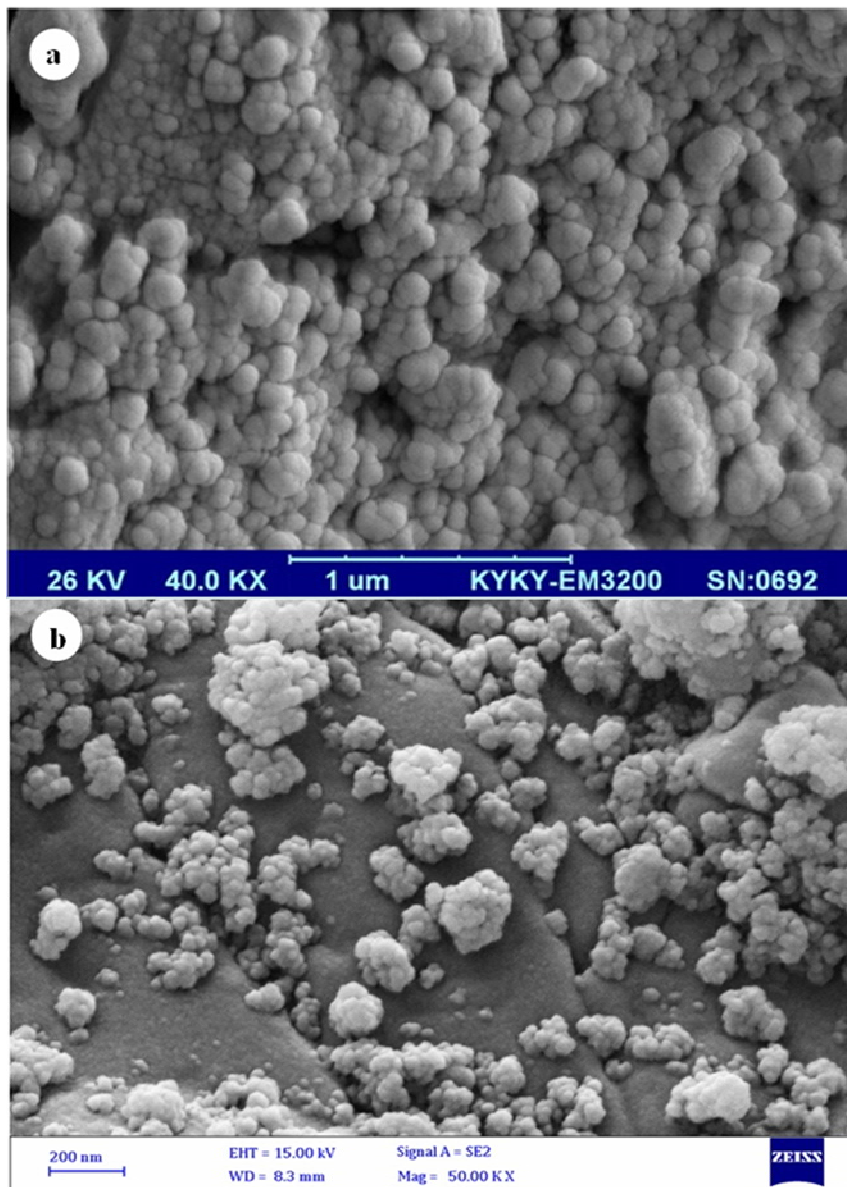


Fig. 5. SEM images of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Propyl-ANDSA}$ before (a) and after (b) the reaction.

to excellent yields. It was observed that substituted aromatic amines with electron-withdrawing groups require longer reaction times with lower yield (entry 3c) in comparison to those with electron-donating groups (entry 3a). Also, by considering steric aspects, it was observed that naphthalen-2-amine require longer reaction time in comparison to aniline.

Literature surveys revealed that various catalysts such as CAN, $\text{Fe}_3\text{O}_4@\text{PEG400-SO}_3\text{H}$, silica sulfuric acid and enzyme-catalyzed were employed in this reaction as demonstrated in Table 3. It is obvious from the results that the products have been obtained in high yields within shorter reaction times in the current work in comparison

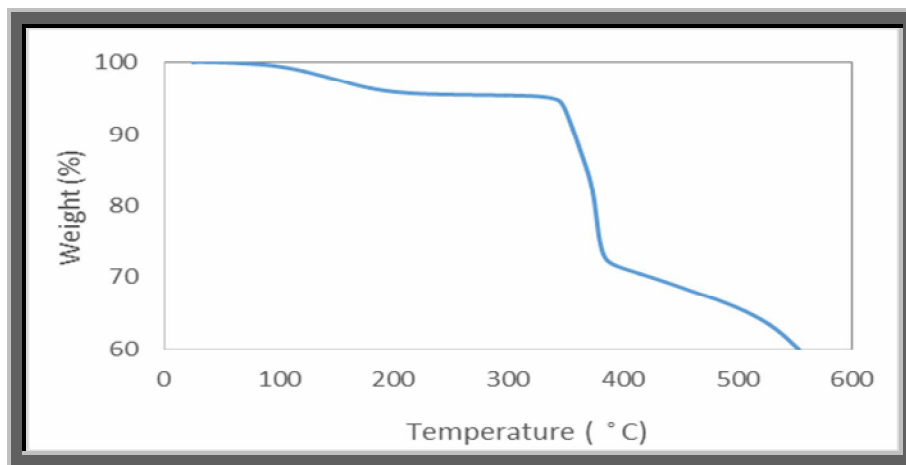


Fig. 6. TGA curve of Fe₃O₄@SiO₂@Propyl-ANDSA.

with other reported procedures. Therefore, the use of Fe₃O₄@SiO₂@Propyl-ANDSA can significantly improve the product yields and decrease reaction time.

RECYCLABILITY OF CATALYST

The recyclability of Fe₃O₄@SiO₂@Propyl-ANDSA was evaluated in the model reaction (Fig. 3). The catalytic activity and reusability of Fe₃O₄@SiO₂@Propyl-ANDSA were tested up to five consecutive cycles for the synthesis of 2,5-dimethyl-1-phenyl-1*H*-pyrrole 3b showing a slight loss of activity even after five cycles (92, 90, 89, 87 and 86 respectively). It is assumed that leaching and degradation of catalyst during recycling have led to a reduction in catalyst activity. After completion of the reaction, the catalyst was recovered by washing with acetonitrile and then dried at 50-60 °C in an oven which was used for five times, and the amount of catalyst used was 0.05 g.

The proposed mechanism in the presence of Fe₃O₄@SiO₂@Propyl-ANDSA is shown in Scheme 2. It is likely that this catalyst has released H⁺, which can act as an electrophilic species. The initiation step begins with the protonation of hexane-2,5-dione, which in condensation with aniline results in the formation of compound 3. Next, aromatization and removal of water from this intermediate result in the final ring system. [9,12,17].

The catalyst was analyzed by different methods such as scanning electron microscopy (SEM), transmission electron

microscopy (TEM), FT-IR spectroscopy, energy-dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA) and vibrating sample magnetometry (VSM) confirming the successful synthesis of Fe₃O₄@SiO₂@Propyl-ANDSA. Also, the catalyst was characterized by the reaction to compare with its structure before reaction. Fe₃O₄@SiO₂@Propyl-ANDSA was collected after the reaction and subjected to different analyses. The EDX spectra of the catalyst before and after reaction are shown in (Fig. 4). The EDX spectra of the catalyst before and after reaction were almost identical indicating that there was no obvious change in the catalyst composition after the reaction. In both spectra, the peaks related to O, Si, and Fe elements are present, and the characteristic peaks of S and N in Fig. 4 indicate that the iron oxide nanoparticles have been successfully coated with ANDSA.

The surface morphology of Fe₃O₄@SiO₂@Propyl-ANDSA was characterized from the electronic scanning microscopy (SEM) technique, as shown in Fig. 5. It shows that these nanoparticles are nearly spherical with nano-dimension ranging from 41.5-94.1 nm in size and a smoother surface.

Figure 5 displays the SEM images of the catalyst before and after the reaction revealed the maintenance of the morphology of nearly spherical nanoparticles with nanometric dimensions after the reaction.

In order to determine the amount of ANDSA loaded on

the surface of Fe₃O₄@SiO₂@Propyl, we measured the percentage of sulfur in Fe₃O₄@SiO₂@Propyl-ANDSA and Fe₃O₄@SiO₂@Propyl through elemental analysis. Using the obtained data in blew tables, the calculated amount of ANDSA loaded on the Fe₃O₄@SiO₂@Propyl is 6.48% (Tables 3 and 4).

The thermo-gravimetric analysis (TGA) curve of the Fe₃O₄@SiO₂@Propyl-ANDSA shows the mass loss of the organic materials as they decompose upon heating (Fig. 6). The TGA curve of the Fe₃O₄@SiO₂@Propyl-ANDSA was divided into several regions corresponding to different mass lose ranges. The first region, situated below 200 °C, displayed a mass loss that was attributed to the loss of the trapped water or adsorbed solvent from the catalyst. The weight loss at (346-385 °C) could be mainly attributed to the evaporation and subsequent decomposition of SO₃H groups.

CONCLUSIONS

In summary, herein we have developed a simple procedure for the synthesis of novel substituted pyrrole derivatives from the Pall-Knorr reaction of various primary amines and 2,5-hexane-dione. Magnetic nanoparticles supported with functionalized 7-aminonaphthalene-1,3-disulfonic acid-functionalized silica (Fe₃O₄@SiO₂@Propyl-ANDSA) were evaluated as an efficient catalyst in this reaction. The promising advantages of the present methodology are generality, efficiently, high yield, short reaction times, easy purification and reusability of the catalyst.

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