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ARTICLE

Functionalized multi-walled carbon nanotubes as an efficient reusable heterogeneous catalyst for green synthesis of *N*-substituted pyrroles in water

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In this protocol, the functionalization of multi-walled carbon nanotubes (MWCNTs) was carried out and the resulted sulfonated MWCNTs characterized by FT-IR, XRD, SEM, BET, EDX, XPS and Raman spectroscopy that each separately discussed in the text. Then, the MWCNTs-SO_3H was applied as an efficient, recyclable heterogeneous catalyst for synthesis of *N*-substituted pyrroles via the reaction of 2,5-dimethoxy tetrahydrofuran with primary amines under clean and mild conditions. In this reaction, the *N*-substituted pyrroles were obtained as benefit and significant products in short reaction times (30-65 min) and good to excellent yields (40-92 %) with high purity. The products were obtained through a simple work up procedure and characterized by FT-IR, ^{1}H NMR and ^{13}C NMR. After the end of reaction, the nanocatalyst was recovered and reused several times without efficient loss of its activity for the preparation of *N*-substituted pyrroles.

Introduction

Since carbon nanotubes have detected by Iijima in 1991, they have received remarkable attention. These elongated tubular macromolecules, including of carbon hexagons regular in a concentric procedure with both ends normally capped by fullerene-like structures, can be seen as a graphite sheet rolled into a nanoscale tubular form single-wall carbon nanotubes (SWCNTs) or with additional graphene tubes around the core of a SWCNT, multi-wall carbon nanotubes (MWCNTs)[1].

Functionalized carbon nanotubes presentation vast potential as components of sensors and nanoscale electronics. The panorama of these applications has led to successful functionalization of single wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) [2–10]. Chemical modification of CNTs is a method employed to increase their applications. Different methods such as chemical behaviour using high concentration acids[11,12], wrapping, sheathing or grafting the CNTs with polymer chains [13–16] and functionalization in plasma conditions [17–19] have been used to better functionalities of CNTs surfaces. Chemical oxidation of nanotubes is generally obtained using gaseous or liquid oxidants. A more general procedure used for CNTs oxidation is the usage of aqueous solutions of oxidizing agents. The oxidation of MWCNTs using acid-sonication has been studied by Xing et al., who demonstrated that the dispersion stability and solubility of the treated MWCNTs in water, improved significantly [20]. Ozone in the presence of an oxidative ozonide cleavage reagent (H_2O_2) has been described as a good oxidizing agent [21]. Some methods for sulfonating of nanotubes have been reported by hydrothermal and microwave assisted under various conditions [22-26].

The substituted pyrroles are a major class of heteroaromatic molecules that are components in a diversity of biologically active natural products and industrially useful compounds.
Pyrroles are present in different bioactive drug molecules such as immunosuppressant, anti-inflammatory and antitumor agents [27]. In view of their high importance, many methodologies have been developed for the structure of the pyrrole [28].

Among them, the Paal–Knorr [29] synthesis reminds the most useful preliminary method for the produced pyrroles. Some of the catalysts have been utilized in these methods are such as; glacial acetic acid [30], P_2O_5 [31], $FeCl_3.7H_2O$ [32], TfOH [33] and *β*-cyclodestrin [34].

In continuation of our previously research on catalytic reactions for synthesis of heterocyclic compounds[35,36] herein, we hope to report efficient sulfonation of MWCNTs and the application of resulted MWCNTs-SO_3H as heterogeneous catalyst for synthesis of *N*-aryl pyrroles. These heterocycles were produced through treatment of 2,5-dimethoxy tetrahydrofuran and various primary aromatic amines in water as a green media.

Experimental

General information

All commercially available reagents were used without further purification and purchased from the Merck Chemical Company in high purity. The used solvents were purified by standard procedures. IR spectra were obtained as KBr pellets on a Perkin–Elmer 781 spectrophotometer and on an impact 400 Nicolet FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ and d_6-DMSO solvents on a Bruker DRX-400 spectrometer with tetramethylsilane as internal reference. Uv-vis spectra were recorded with a Perkin-Elmer 550 spectrophotometer in CH_2Cl_2 solvent. The nanostructures were characterized using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuK, radiation, k= 0.154056 nm), at a scanning speed of 2°/min from 10° to 100° (2Ø). The morphological study of nanocomposites was investigated by a scanning electron microscopy (SEM, Leo 1455VP). Electron

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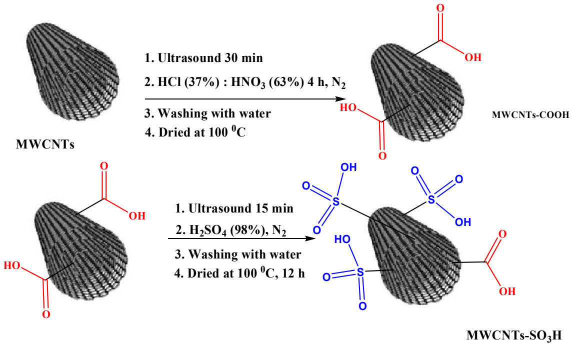
Dispersive X-Rey (EDX) of catalyst was performed on a Philips Holland model XL30. The surface area analysis (BET) was performed by using an automated gas adsorption analyzer (NANO SORD). The Raman spectra were recorded with an Almega Thermo Nicolet Dispersive Raman spectrometer excited at 532 nm. X-ray photoelectron spectroscopy (XPS) spectra were measured on an ESCA-3000 electron spectrometer with non-monochromatized Mg Kα X-rays as the excitation source. Melting points were obtained with a Yanagimoto micro melting point apparatus are uncorrected. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

General procedure for the synthesis of MWCNTs-SO_3H

Preparation of MWCNTs-SO_3H catalyst was performed in two steps as described in Scheme 1. MWCNTs (1g) and deionized water (100 ml) were added in a becher and it sonicated for 30 min. After sonication, the solvent was removed in vacuum and the obtained MWCNTs were transmissive to another flask including 25 ml HNO_3 (63%), 25 ml HCl (37%) and stirred at 80 °C for 4 h under a nitrogen atmosphere. Then, the solution was filtered in vacuum and washed throughout with deionized water and dried at 100 °C for 10 h. In this step, the MWCNTs-COOH was obtained. The MWCNTs-COOH (1g) and deionized water (50 ml) was sonicated for 15 min. Then, the water was filtered and MWCNTs-COOH was dried. Then, 40 ml H_2SO_4 (98%) was added to the set-up at 250-270 °C for 20 h under a nitrogen atmosphere. After cooling the solution, the liquid was filtered and washed throughout with deionized water for several times. The obtained solid dried at 100 °C for 12 h. After this step, the MWCNTs-SO_3H was obtained and used as a catalyst in the synthesis of *N*-aryl pyrroles.



Scheme 1. Preparation of MWCNTs-SO_3H catalyst

General procedure for the synthesis of N-aryl pyrroles

To a mixture of 2,5-dimethoxy tetrahydrofuran (1.2 mmol) and different primary aromatic amines (1mmol) in water (5 ml) as solvent was added the MWCNTs-SO_3H (0.04 g) as a catalyst. Then, the reaction mixture was heated (80°C) and stirred at different times in water. The progress of the reactions was monitored by TLC (ethyl acetate/*n*-hexane 6/4). After the completion of reaction, the catalyst along with solid product was collected by filtration from the reaction mixture. The filtrated solid was dissolved in chloroform, the separated catalyst from the reaction mixture, washed with chloroform. The solvent was removed in vacuum to give the crude product. Then, the crude product was recrystallized from ethanol, *N*-aryl pyrroles were obtained as pure products. The recovered catalyst (0.019 g) was reused in the reaction for 4 runs. All of the pure products were characterized by comparison of their physical and spectral data with authentic samples [37-47].

Results and discussion

Preparation and characterization of catalyst

In the first step, the MWCNTs were converted to MWCNTs-COOH with HCl (37%) and HNO_3 (63%). This step was carried out in order to purity of MWCNTs and to remove fullerene, amorphous carbon and catalyst particles such as Fe, Co, Ni and increase the reactivity. This step also introduced oxygen comprising groups, mainly carboxyl groups on the MWCNTs [48,49]. After this step, the sulfuric acid (98%) was added to MWCNTs-COOH to obtain the MWCNTs-SO_3H.

The prepared catalyst was characterized by SEM, EDX, XRD, FT-IR, BET, XPS and Raman spectroscopy. The spectroscopic data of FT-IR was confirmed that the functionalization of MWCNTs with sulfonic acids groups is occurred (Fig. **1-a,b**).

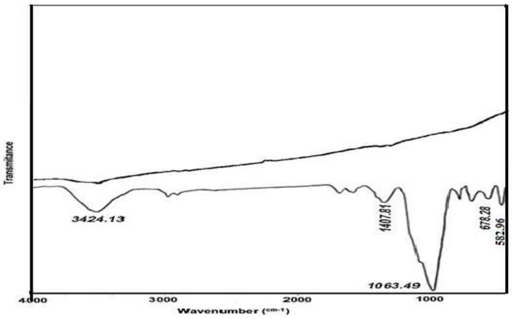


Fig. 1. **a**) FT-IR spectra of MWCNTs **b**) FT-IR spectra of MWCNTs-SO_3H

This spectrum shows peaks at about 1400 and 1100 cm^{-1} which corresponds to the SO_2 asymmetric and symmetric stretching modes, respectively. In addition, in the low frequency part of spectrum, the line at 670 cm^{-1} was assigned to the S-O stretching mode and the peak shown at 582.96 cm^{-1} was assigned to the C-S stretching mode, suggesting the existence of covalent sulfonic acid groups. The broad band centred at about 3400 cm^{-1} is the contribution of acidic OH. The XRD images of MWCNTs before and after the H_2SO_4 treatment are shown in Fig. 2-**a, b**. As can be seen in Fig. 2, the XRD pattern for MWCNTs (Fig. **2a**) has slightly difference in peak width than peak related to MWCNTs-SO_3H (Fig. **2b**) suggesting the structure of MWCNTs was not changed after the functionalizing to MWCNTs-SO_3H.

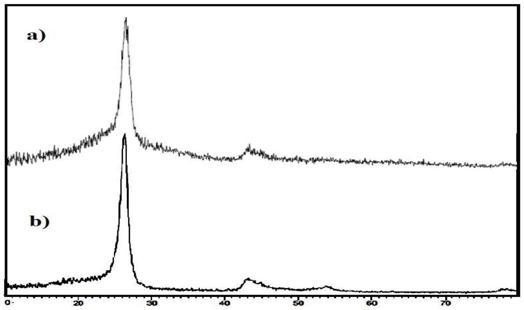


Fig. 2. **a**) XRD spectra of pristine MWCNTs **b**) XRD spectra of MWCNTs-SO_3H

The SEM images of MWCNTs before and after the H_2SO_4 treatment are shown in Figure 3. Compared with the primitive MWCNTs and the MWCNTs-SO_3H were covered by a layer and there are severely entangled and form big agglomeration that resulting in thickened MWCNTs. Also, the EDX image of the MWCNTs-SO_3H is shown in Figure 4. For MWCNTs@SO_3H, the results obtained by EDX were as follows (%): C, 95.80; O, 1.73; S, 2.47. This image was confirmed the oxygen and sulphur contain regarding to the functionalized MWCNTs. Furthermore, the EDX image infers that functional groups such as sulfonic acid were attached to the MWCNTs.

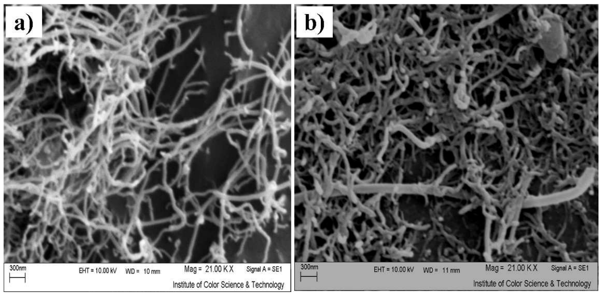


Fig 3. a) SEM images of MWCNTs b) SEM images of MWCNTs-SO_3H

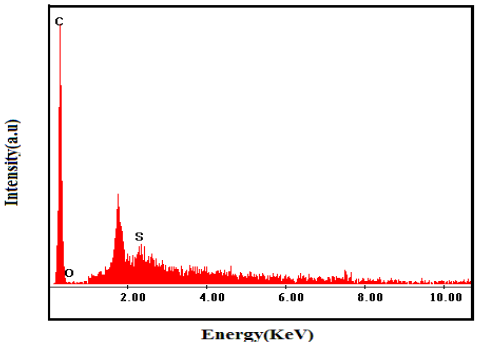


Fig 4. The EDX pattern of MWCNTs-SO_3H catalyst

Another technique is used to characterize MWCNTs is Raman spectroscopy. In the region spectrum (1300-1600 cm^{-1}), two bands are observed showing the characteristic of MWCNTs. These bands point the graphite band (G-band) and disorder and defects of the structure, named (D-band). The ratio between the intensity of the D-band and the G-band, noted I_D/I_G value, corresponds to a higher proportion of sp^3 carbon atoms. Figure 5 shows the Raman spectra of MWCNTs and MWCNTs-SO_3H. As shown in Figure 5a, the spectrum exhibit two peaks at about 1345 and 1583 cm^{-1} that the feature in 1583 cm^{-1} is G-band and the origin of the line at 1345 cm^{-1} is D-band regarding to MWCNTs. Also, in Figure 5b, two peaks at 1349 and 1583 cm^{-1} are D-band and G band of MWCNTs-SO_3H, respectively. It was calculated that the I_D/I_G values of MWCNTs and MWCNTs-SO_3H are 0.85 and 1.70, respectively. This increasing the ID/IG value points that some of the sp^2 carbon atoms were converted to sp^3 carbon atoms on the side walls of MWCNTs. This matter can be related to the functionalization of MWCNTs by sulfonic acid groups.

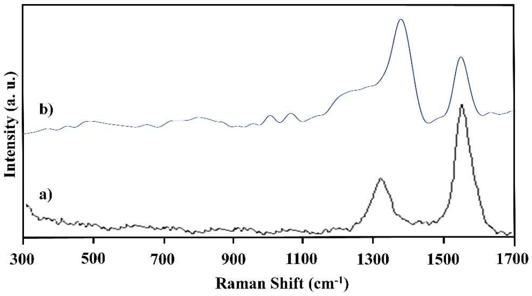


Fig 5. Raman spectra of a) MWCNTs b) MWCNTs-SO_3H

XPS spectra were employed to investigate the chemical valences of functional groups attached to the surface of MWCNTs. As shown in Figure 6, the spectra of C1s region, O1s region and S2p region were assigned. The main peak appears at 284.9 eV with a non-symmetrical edge. This peak generally referred as the sp^2 carbon-carbon double bond or sp^3 carbon-carbon single bond[50]. Also, this peak is related to the sp^2-hybridized graphite carbon. The peak at 288.7 eV can be determined as carbon atoms bound with oxygen or sulphur in functionalized groups e.g. carboxylic acid or sulfonic acid groups [50]. The O1s region shows that all the peaks take place in the range of 530.9 to 534.2 with peak maxima at ~533.1 eV.[22] In the S2p region, the main peak of sulphur in the sulfonic acid groups was observed at 169.2 eV. The peak at 169.2 eV is related to a higher oxidation state of sulphur in SO_3H groups.[22]

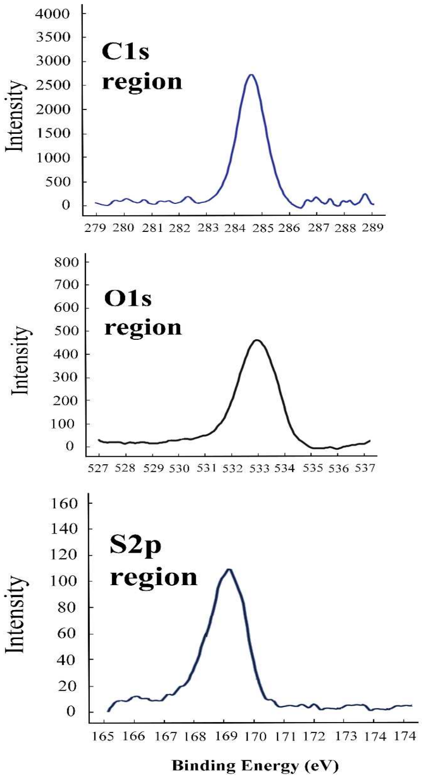


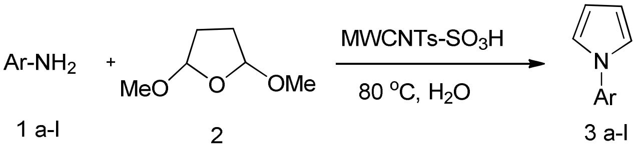
Fig 6. The XPS spectra of MWCNTs-SO_3H in the region of C1s, O1s, and S2p

The surface area of the initial MWCNTs and MWCNTs-SO_3H as a target solid catalyst was determined by BET technique. The corresponding results were indicated in Table 1. The decrease of the total and unit surface of MWCNTs after sulfonation was approved the presence of -SO_3H as acidic groups on the surface of solid catalyst (Table 1). It can be concluded that the sulfonation of carbon nanotubes was take placed, because the physically adsorption of nitrogen gas after functionalization using sulphuric acid was decreased. This is nearly 50% lower than the raw MWCNTs

Table 1. Surface area of MWCNTs and MWCNTs-SO_3H

Name	S.A(BET) (m^2/g)	S.A(Total) (m^2)
MWCNTs	62.775	0.816
MWCNTs-SO_3H	30.925	0.619

In order to investigate the catalytic activity of MWCNTs-SO_3H and compared with other catalysts was occurred. The reaction of 2,5-dimethoxy tetrahydrofuran with 4-methoxy aniline as 1.2:1 mole ratio was done in the presence of various catalysts under thermal conditions in water as solvent. It was found that the reaction in the presence of $CuFe_3O_4$, Fe_3O_4, TiO_2, ZnS nano particles, MWCNTs, MWCNTs-COOH, MWCNTs/H_2SO_4 and Ph-SO_3H, the products have not suitable yields (Table 2). While, the reaction in the presence of MWCNTs-SO_3H as a heterogeneous catalyst in the same conditions to achieve the appropriate results on the basis of yield and reaction time (Table 2, entry 5). Then, the reaction was carried out in the presence of MWCNTs-SO_3H (Scheme 2).



Scheme 2. Reaction of 2,5-dimethoxy tetrahydrofuran and primary aromatic amines

Table 2. Investigation of the different catalysts under 80°C in water

Entry	Catalyst	Time (h)	Yield (%)
1	$CuFe_2O_4$	12	40
2	Fe_3O_4	5	30
3	TiO_2	12	-
4	ZnS	8	-
5	MWCNTs-SO_3H	1	30
6	MWCNTs	7	-
7	MWCNTs-COOH	5	10
8	MWCNTs/H_2SO_4 (A drop)	5	-
9	Ph-SO_3H	3	17

Then, the optimization of catalyst amount in the reaction was occurred. The reaction of 2,5-dimethoxy tetrahydrofuran with 4-methoxy aniline with 1.2:1 mole ratio was occurred in different concentrations of catalyst under thermal conditions in water. The corresponding results are presented in Table 3. By consideration of the results in Table 3, the optimum amount of used MWCNTs-SO_3H as a catalyst in this reaction was obtained 0.04 g per one mol of aniline derivative (Table 3, entry 4).

Table 3. Optimization of the catalyst amount at 80°C in water

Entry	Amounts of catalyst (g)	Time (min)	Yield (%)
1	0.01	120	30
2	0.02	120	45
3	0.03	90	60
4	0.04	45	92
5	0.05	45	92

After the optimization of catalyst amount, the reaction was carried out in various solvents (Table 4). The best results were obtained using water as solvent (Table 4, entry 4). Then, the reaction of 2,5-dimethoxy tetrahydrofuran with 4-methoxy aniline (1.2:1 mole ratio) in the presence of MWCNTs-SO_3H catalyst (0.04 g) in water solution, was occurred in various temperature (Table 5). The best results were obtained at 80°C (Table 5, entry 3).

Table 4. Optimization of different solvents in the presence of MWCNTs-SO_3H (0.04 g) at 80°C

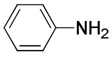
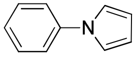
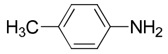
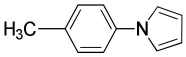
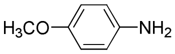
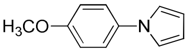
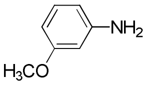
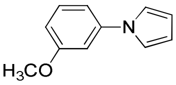
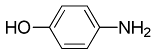
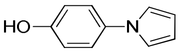
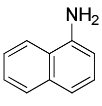
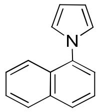
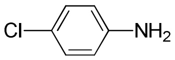
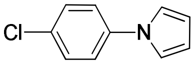
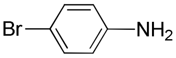
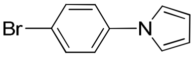
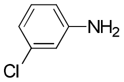
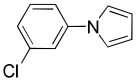
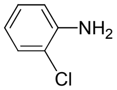
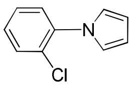
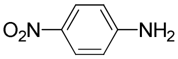
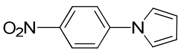
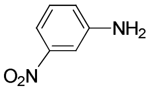
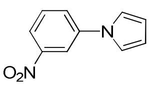
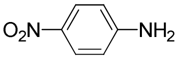
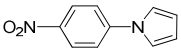
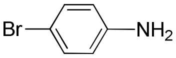
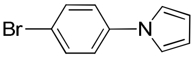
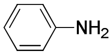
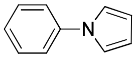
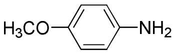
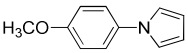
Entry	Solvent	Time (min)	Yield (%)
1	EtOH	30	5
2	CH_3CN	30	40
3	DMF	30	80
4	H_2O	30	90

Table 5. Optimization of temperature in the presence of MWCNTs-SO_3H (0.04 g) in water

Entry	Temp. (^{0}C)	Time (min)	Yield (%)
1	60	45	70
2	70	45	83
3	80	45	92
4	90	45	90
5	100	45	87

In ascertain and limitation of this protocol, the reaction of 2,5-dimethoxy tetrahydrofuran with several primary aromatic amines was carried out according to the general experimental procedure. The corresponding products and their results are summarized in Table 6. In this study, *N*-aryl pyrroles as products in an efficient method were prepared through the reaction of 2,5-dimethoxy tetrahydrofuran and various primary aromatic amines in the presence of heterogeneous catalytic amount of MWCNTs-SO_3H (0.04 g) under thermal conditions in water. A comparison of the present method with the previously works using other catalysts was done and the related results were indicated in the Table 6, entries 13-16 [37,51].

Table 6. Synthesis of various *N*-aryl pyrroles using MWCNTs-SO_3H (0.04 g) as catalyst under thermal conditions (80°C) in water

Entry	Amine	Product	Time (min):Yield (%)[a]
1			45:88
2			50:89
3			45:92
4			50:87
5			30:92
6			30:90
7			55:88
8			50:88
9			55:78
10			65:40
11			60:72
12			60:70
13[b]			720:62
14[b]			360:66
15[c]			10:70
16[c]			10:77

[a] Isolated yields

[b] The reaction conditions: 10% MgI_2 $(OEt_2)_n$, CH_3CN, 80°C, Lit.[51].

[c] The reaction conditions: AcOH, MW, 170 °C, Lit.[37].

Recycling of the catalyst

For practical applications of heterogeneous catalysts, the life-time of the MWCNTs-SO_3H and its level of reusability are very important features. At the end of each reaction, the catalyst was isolated by filtration, washed exhaustively with chloroform and ethanol, and dried at 100 °C for 24 h before being used with fresh materials. The catalyst was reused for 4 runs; the yields were ranged from 95% to 90% (Fig. 7).

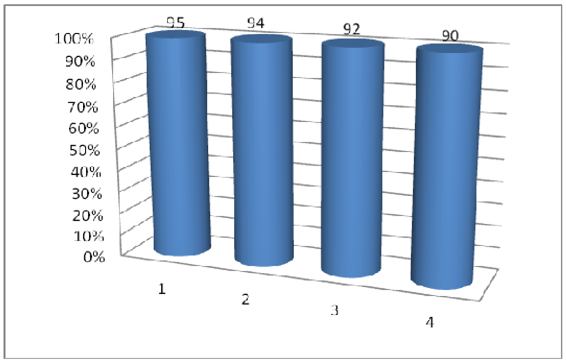


Fig. 7. Reusability of the catalyst in the reaction

The structures of N-aryl pyrroles as products were confirmed by physical and spectroscopic data such as; melting point, IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra of 1-(3-nitrophenyl)-1H-pyrrole is shown the signals around δ=6.33-7.34 ppm that is assigned to the protons of the aromatic rings (Fig. 8). In the ^{13}C NMR spectra of the above mentioned compound is shown the signals around δ=110.0-150.0 ppm that is assigned to the carbon atoms of the aromatic rings (Fig. 9).

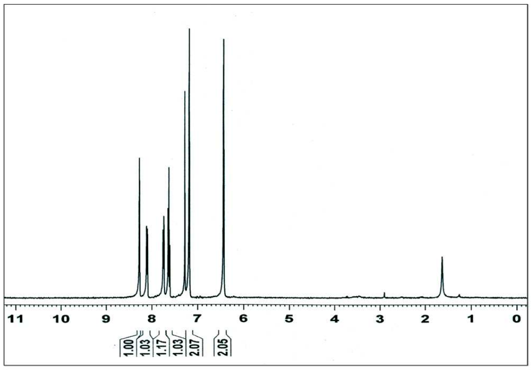


Fig. 8. ^{1}H NMR spectrum of 1-(3-nitro phenyl)-1H-pyrrole

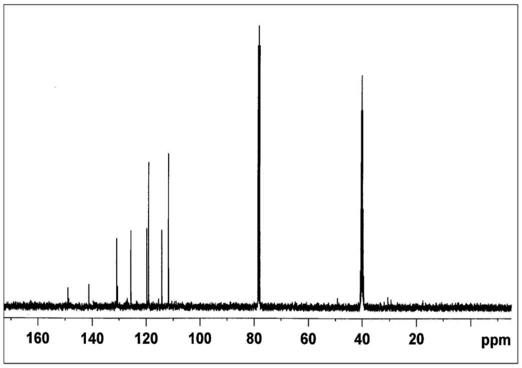
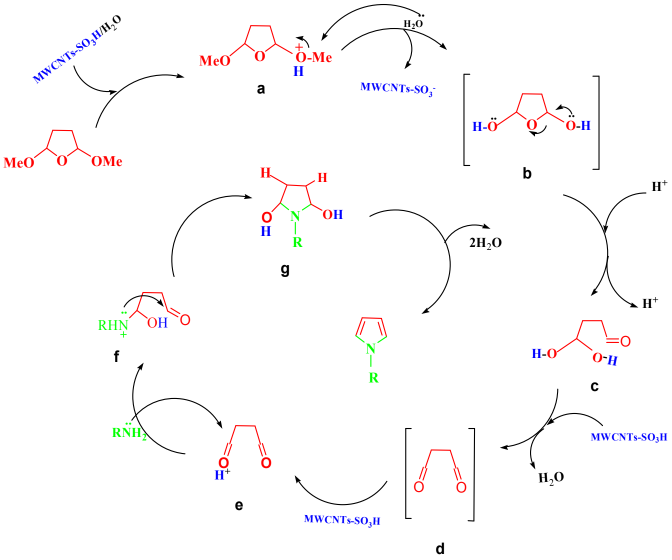


Fig. 9. ^{13}C NMR spectrum of 1-(3-nitro phenyl)-1H-pyrrole

A plausible mechanism[52] for the formation of *N*-aryl pyrroles is presented in Scheme 3. As can be seen, in the first step, it was protonated acetal group of 2,5-dimethoxy tetrahydrofuran compound **a**. Then, the nucleophilic attack of hydroxyl group of the substrate to the carbon atom of acetal to produce the intermediate **b**. Next, the **b** was protonated by MWCNTs-SO_3H and dehydrated to convert into the dicarbonyl compound (**d**)**.** Also, **d** was protonated by MWCNTs-SO_3H, then nucleophilic attack of amino group to carbonyl group of **e** to produce **f.** Finally, the **f** was protonated, cyclized and dehydrated to give *N*-aryl pyrrole as a desired product.



Scheme 3. Plausible reaction mechanism for preparation of *N*-aryl pyrroles

Conclusion

In this research, it was described the synthesis of N-aryl pyrroles using 2,5-dimethoxy tetrahydrofuran with different primary aromatic amines. This reaction was performed in the presence of catalytic amount of MWCNTs-SO_3H (0.04 g) under thermal conditions. The corresponding products have been obtained in excellent yields, high purity and short reaction times. The products have been confirmed by physical and spectroscopic data such as; melting point, FTIR, ^1H NMR, ^{13}C NMR spectroscopy.

Acknowledgments

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