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ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2015, Vol. 31, No. (2):
Pg. 733-739

Covalently Supported Sulfonic and Acetic Acids onto Polypyrrole Asgreen, Cheap and Recoverablesolid Acid Catalysts for the synthesis of 4*H*-pyrano[2,3-c]pyrazoles

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http://dx.doi.org/10.13005/ojc/310215

(Received: January 12, 2015; Accepted: March 18, 2015)

ABSTRACT

Sulfonated polypyrrole nanospheres and polypyrrole N-functionalized acetic acid were synthesized. The catalytic efficiency of the prepared solid acid catalysts for the synthesis of 4Hpyrano[2,3-c]pyrazoles derivatives was evaluated and compared. The results showed that, regarding the time and yield of the products, the sulfonatedpolypyrrolenanospheres catalyst has better catalytic activity than polypyrrole N-functionalized acetic acid during first andsecond runs but shows a slight decline in its activityduring thethird run.

Key words: Sulfonated polypyrrole nanospheres.

INTRODUCTION

Heterogenization of homogeneous catalysts has been an interesting area of research from the industrial point of view; this combines the advantages of homogeneous catalysts (high activity and selectivity, *etc.*) with the engineering advantages of heterogeneous catalysts such as easy catalyst separation, long catalytic life, easy catalyst regenerability, thermal stability and recyclability.[1] Several types of solid sulfonic acid functionalized silica (both amorphous and ordered) have been synthesized and applied as an alternative to traditional sulfonic acid resins and homogeneous acids in catalyzing chemical transformations.[2-5]From this viewpoint, catalytic reactions lead to valuable

processes, since theuse of stoichiometric reagents that are often toxic pose essential restrictions from both an economical and an environmental standpoint and havedirect relation to product purification and waste controlling.[6]Use of solid acids in organic reactions has significant roles, because these species have many rewards such as ease in handling, reduced reactor and plant corrosion harms, and more environmentally benign disposal[7–12]. Green chemistry not only needs the use of environmentally benign reagents and solvents, but also the recovery and reuse of the catalyst. Fromthis perspective, some types of solid sulfonic acid functionalized silica have been synthesized and used as an alternate to traditional homogeneous acids in catalyzing chemical transformations.

Recently, nanotubular and nanosphere conducting polymers have attracted much attention due to their interesting electrochemical properties caused by their small dimensions and high surface area.[13–16] Among the reported conducting nanopolymers, polypyrrole nanotubes (PPyNTs) and polypyrrole nanospheres (PPyNs) have received attractiveness because of redox properties, their relatively high conductivity, easy preparation, ion exchange capacity, excellent environmental stability.[17-19]Moreover, PPyNTs and PPyNs can be synthesized chemically in a bulk amountfrom benign aqueous environment in ambient conditions, without the use of high technology and sophisticated instruments.

Pyrano[2,3-c]pyrazoles establish important precursors to hopeful drugs in the field of medicinal chemistry and exhibit wide range of biological activities.[20–22] Therefore, development and improvement of new synthetic approaches in this field using easily accessible and benign catalysts seems to be a remarkable challenge. These compounds were first obtained by H. Otto in 1974 by adding malononitrile to 4-arylidene-3-methyl-2-pyrazolin-5-one.[23] Several methods have been described for the preparation of this class of compounds.[24-35] However, many of these methods suffer from certain drawbacks such as low yield, harsh reaction conditions, prolonged reaction time, and application of hazardous and/or costly catalysts and solvents. Therefore, development of greener, clean, and environmentally friendly approaches is still in demand. Due to the importance of pyrano[2,3-c]pyrazoles compounds, herein, we wish to introduce sulfonatedpoly pyrrole nanospheres and polypyrrole N-functionalized acetic acid as new efficient and recyclable catalysts for one-pot three-component synthesis of highly functionalized 4*H*-pyrano[2,3-c]pyrazoles**2a–s** from the reactions between aldehydes **1**, malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one.

MATERIAL AND METHODS

General

Products were characterized by comparison of their spectroscopic data (^{1}HNMR, ^{13}CNMR and IR) and physical properties with those reported in the literature. NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ on Bruker Advanced DPX 400 MHz instrument spectrometers using TMS as internal standard. IR spectra were recorded on a BOMEMMB-Series 1998 FT-IR spectrometer. ultrasonicator (Elma Transsonic T460/H) was used for ultrasonication. All yields refer to isolated products.

Preparation polypyrrole nanospheres (PPyNs)

In a typical procedure, in a round bottom flask containing 120 ml of deionized water, 4.0 g of decyl alcohol (1-decanol, 99%, Aldrich) was added and the mixture was stirring at room temperature for 40 min. Then, 6.0 g of dodecyltrimethyl ammonium bromide (DTAB, 99%, Aldrich) was added. After further stirring at 0°C for 30 min, the emulsion was moved to an ultrasonicator (Elma Transsonic T460/H of capacity 1.5 liters and frequency of 35 kHz). Then, 3.2 g of pyrrole (98%, Aldrich) was added drop-wise to the mixture. To initiate polymerization, 8.0 g of $FeCl_3$ (99%, Aldrich) was added. After ultrasonication for 3 h, the solid PPyNs were separated by filtration, washed with ethanol to remove the surfactant, and dried in an oven at 60°C overnight.

Preparation of sulfonated Polyperrole nanospheres (SPPyNs)

PyPNs (0.5 g) was heated in 100 ml of concentrated H_2SO_4 at 150°C for 4 h. After cooling down to room temperature, ethanol (1000 ml) was added. The black solid was collected by filtration, and washed repeatedly using ethanol until no sulfate ions were detected in the filtrate.[36]

Preparation of Polyperrole nanotubes (PPyNTs)

The synthesis of PPyNTs was carried out

by a self-degraded template method as reported in the literature.[38]In a typical procedure, 0.24 g (1.5 mmol) of $FeCl_3$ was dissolved in 30 mL of 5 mM MO solution (0.15 mmol). Pyrrole monomers (105 mL, 1.5 mmol) were then added and the mixture was stirred at room temperature for 24 h. The formed PPy precipitate was washed with deionized water/ethanol several times until the filtrate was colourless and neutral. The produced PPyNTs was finally dried in dynamic vacuum at 60 °C for 24 h.

Preparation of Polyperrole nanotubes N-functionalized acetic acid (PPyNTsAA)

A mixture of PPyNTs (0.1 g), KOH powder (0.15 g), was dispersed in 25 mL DMF and sonicated for 1hand ethyl chloroacetate (0.61 g, 5 mmol) was added and then held at 60°CC for 12 h under vigorous agitation. Then HCl (20%) was added until the *P*H of the mixture decreased to 5 and heated again at 60 æ%C for another 2 h. Finally, the solid black precipitate was filtrated and washed with deionized water and ethanol to thoroughly remove physically absorbed HCl and unreacted ethyl chloroacetate from the surface of PPyNTsAA.

General procedure for synthesis of 4H-pyrano[2,3-c]pyrazolesderivatives

3-methyl-1-phenyl-2-pyrazolin-5-one (1 mmol), aldehyde (1 mmol) and malononitrile (1 mmol), were placed together in a round-bottom flask containing 5 mL of EtOH. SPPyNs (0.01 g) or PPyNTsAA (0.03 g) was added to the mixture and the suspension was magnetically stirred at reflux condition for appropriate time according to (Table 2). After completion of the reaction as followed by TLC (n-hexane: ethyl acetate; 3:1), the catalyst was filtered and washed with hot ethanol (2×5 mL). The recovered catalyst was washed with acetone, dried and stored for other similar consecutive runs. The filtrate mixture was recrystallized to provide the pure crystals of 4H-pyrano[2,3-c]pyrazole derivatives. The products are known compounds and are characterized by IR and NMR spectroscopy data for new compounds. Their melting points are compared with reported values.[24-35]

Spectral data for selected products

6-Amino-4-(4-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1d)

Pale yellow powder; Yield: 0.32g (89%); mp 241-243 °C (242-243 °C). IR (KBr): $\bar{\nu}$ = 3394, 3325, 3059, 2975, 2193, 1661, 1597, 1515, 1397, 1258 cm^{-1}. ^1H NMR: δ = 1.78 (3H, s, CH_3), 3.74 (3H, s, OCH_3), 4.62 (1H, s, CH), 6.89 (2H, d, *J* = 8.5 Hz, 2CH), 7.15 (2H, s, 2CH),7.17 (2H, s, NH_2), 7.31 (1H, t, *J* = 7.6 Hz, CH), 7.49 (2H, t, *J* = 7.6 Hz, 2CH), 7.77 (2H, d, *J* = 8.5 Hz, 2CH) ppm. ^{13}C NMR: δ = 12.6, 35.9, 55.1, 58.6, 98.9, 113.8, 119.9, 120.1, 126.2, 128.8, 129.4, 135.6, 137.5, 145.4, 158.2, 159.3 ppm.

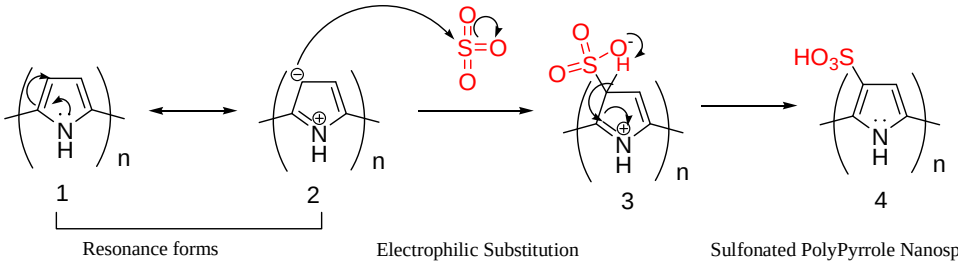
6-Amino-4-(3-nitrophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1e)

Yellow powder; Yield: 0.33g (88%); mp 190-192 °C (189-191 °C). IR (KBr): = 3436, 3296, 3098, 2190, 1651, 1589, 1517, 1446, 1386, 1349, 1258, 1119 cm^{-1}. ^1H NMR: δ = 1.90 (3H, s, CH_3), 4.81 (1H, s, CH), 4.83 (2H, s, NH_2), 7.36-7.37 (1H, m, CH), 7.48-7.51 (2H, m, 2CH), 7.56-7.59 (1H, m, CH), 7.66-7.67 (3H, m, 3CH), 8.13 (1H, s, CH), 8.19 (1H, d, $^3J_{HH}$= 7.2 Hz, CH) ppm. ^{13}C NMR: δ = 13.0, 36.8, 57.6, 98.0, 120.3, 120.5, 122.7, 126.7, 129.7, 130.7, 135.2, 137.9, 144.5, 145.6, 146.4, 184.4, 160.3 ppm.

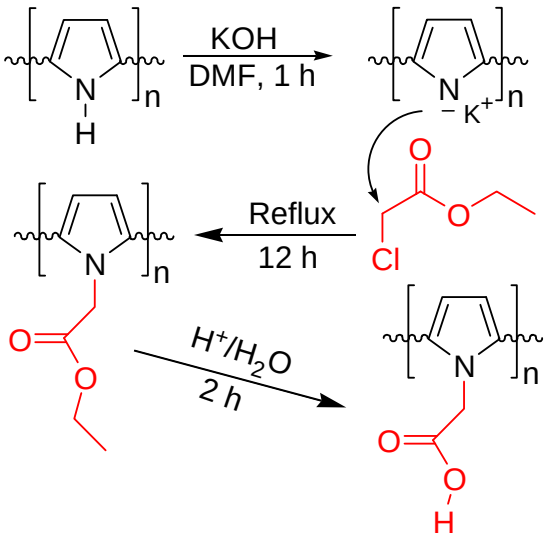
RESULTS AND DISCUSSION

The proposed mechanism followed to obtain sulfonatedPolyperrolenanospheres (SPPyNs) and Polyperrole nanotubes N-functionalized acetic acid (PPyNTsAA) are outlined in scheme 1 and 2.

Figure 1 shows the FESEM image of polypyrrolenanospheres (PPyNs). From figure 1, it can be seen that PPyNs have spherical shapewith an average particle size of around 70-80 nm in diameter. The FESEM image of sulfonatedpolypyrrole nanospheres (PPyNs) shows that the particle surfaces are similar to that before sulfonation but the particles have become smaller in size with an average diameter of about 60-70 nm (Figure 2). The FTIR spectra of the SPPyNs exhibits a peak around 1550 cm^{-1} which is attributed to the C=C stretching vibration of pyrrole.The peaks at 1700 and 1300 cm^{-1} are assigned to C=N and C–N vibrations in PPy.A characteristic peak around 1045 cm^{-1} is attributed to the symmetric O=S=O stretching vibrations and confirms the presence of $–SO_3H$ groups in SPPyNs. Moreover, the peaks at around 800 and 650 cm^{-1} are assignable for S–O and C–S stretching vibrations, respectively.After the 3th reaction run, SPPyNs catalyst still possessed these peaks, indicating a good



Scheme 1: Proposed mechanism for the Preparation of SPPyNs



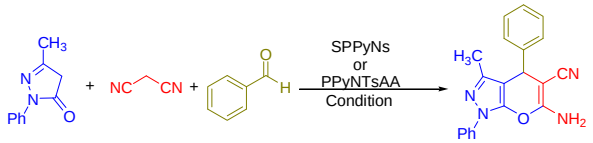
Scheme 2: Proposedmechanism for thePreparation PPyNTsAA

catalyst recyclability of SPPNs.

In order to prepare PPyNTsAA catalyst, a mixture of PPyNTsand KOH powder was dispersed in DMF and sonicated to deprotonatePPyNTs. Then, ethyl chloroacetate was added and then heated at 60 æ%C for 12 h under vigorous agitation. Then aqueous HCl was added until the *P*H of the mixture decreased to 5 and heated again for further 2 h. Finally, the solid black precipitate was filtrated and washed with deionized water and ethanol to thoroughly remove physically absorbed HCl and unreacted ethyl chloroacetate from the surface of PPyNTsAA.

Figure 3 shows the FTIR spectra of PPyNTs and PPyNTsAA. From figure 3b, two characteristic picks confirm the successful supporting of acetic acid on the surface of polypyrrole nanotubes. A newly

Table 1: Investigation of catalytic activity of SPPyNs catalyst for the synthesis of 4*H*-pyrano[2,3-c]pyrazoles under various conditions



Entry	Conditions	t [f C]	SPPyNs (g)	Time (min)	Yield (%) [a]	PPyNTsAA (g)	Time (min)	Yield (%) [a]
1	neat	100	0	60	Trace	0	60	Trace
7	H_2O	reflux	0.005	40	60	0.005	60	50
3	CH_3CN	reflux	0.005	40	63	0.01	40	60
4	THF	65	0.005	45	65	0.01	45	70
5	DMF	100	0.005	35	68	0.01	45	65
6	H_2O/DMF	100	0.005	35	68	0.01	45	70
8	CH_3CH_2OH	reflux	0.005	35	70	0.01	40	70
9	CH_3CH_2OH	reflux	0.010	30	89	0.03	40	87
10	CH_3CH_2OH	reflux	0.015	30	92	0.04	40	88

[a] Yield refer to isolated and pure product

observed characteristic pick at 1635 cm^{-1} is assigned to C=O stretching vibration of carboxylic group, and also a new broad peak between 3000-4000 cm^{-1} is attributed to OH of carboxylic acid.

On the base of our best knowledge, there is only one report that has investigated the catalytic activity of SPPyNs.[36]Moreover; this is the first report on the preparation of PPyNTsAA.Herein; we became interested in investigating the catalytic activity of the prepared SPPyNs and PPyNTsAAas new heterogeneous polymer based acid catalysts for the synthesis of 4*H*-pyrano[2,3-c] pyrazoles derivatives.

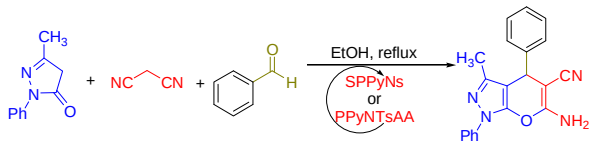
To optimize the reaction conditions, the reaction of the reaction of benzaldehyde, malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one was selected as model to examine the effect of SPPyNs and PPyNTsAA catalysts under a variety of conditions (Table 1).

The present optimization studies revealed that the best results were achieved by caring out the reaction in the presence of 0.01 g of SPPyNs and 0.03 g of PPyNTsAA under reflux condition in ethanol (Table 1,entries 9 and 10). The larger amounts of the catalysts (0.015 g of SPPyNs and o.4 g ofPPyNTsAA) did not improve the yield while decreasing the amount of the catalyst led to decreased yield. Using these optimized conditions, the reaction of aromatic

Table 2: Synthesis of 4*H*-pyrano[2,3-c]pyrazole derivatives catalyzed by SPPyNs and PPyNTsAA

Product	Ar	SPPyNs Catalyst		PPyNTsAA Catalyst	
		Time(min)	Yield (%)[a]	Time(min)	Yield(%)[a]
1a	C_6H_5	30	78	35	80
1b	4-PhC_6H_4	40	81	50	79
1c	4-MeC_6H_4	35	79	40	84
1d	4-$MeOC_6H_4$	40	85	45	81
1e	3-$NO_2C_6H_4$	25	82	30	85
1f	4-ClC_6H_4	30	81	45	89
1g	2,4-$(Cl)_2C_6H_3$	25	89	40	79
1h	4-CNC_6H_4	30	86	50	88
1i	4-OHC_6H_4	45	79	60	84
1j	4-BrC_6H_4	40	80	50	87
1k	2-OHC_6H_4	45	78	60	80

Table 3: Recyclability and reusability study of SPPyNs catalyst



Run	SPPyNs Catalyst		PPyNTsAA Catalyst	
	Time(min)	Yield (%)[a]	Time(min)	Yield (%)[a]
1	30	78	35	80
2	30	80	35	79
3	40	75	35	81

[a] Isolated yield

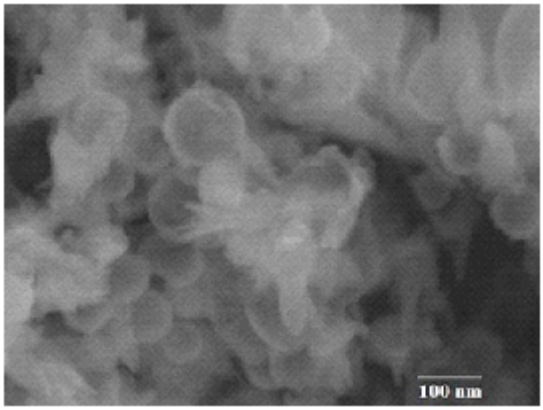


Fig. 1: FESEM images of Polyperrole nanospheres (PPyNs)

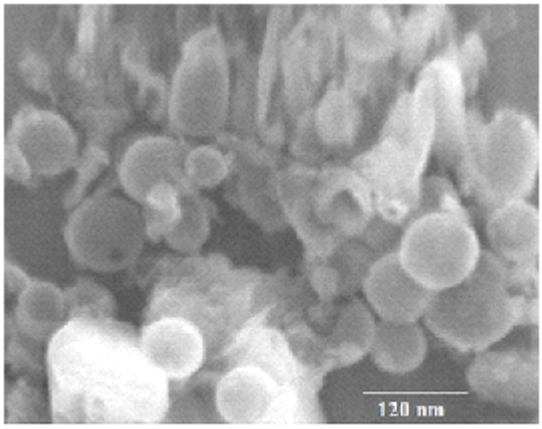


Fig. 2: FESEM images of sulfonated Polyperrole nanospheres (SPPyNs)

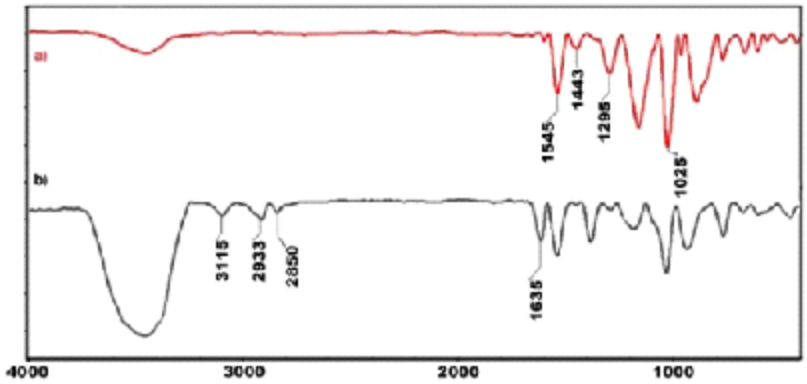


Fig. 3: FTIR spectra of (a)PPyNTs and (b) PPyNTsAA

aldehydes, malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one was explored (Scheme 3).

Table 2 represents the reaction times, Yields and the product of different synthesized 4*H*-pyrano[2,3-c]pyrazole derivatives from various substrates using SPPyNsand PPyNTsAA as catalysts. All the products were cleanly isolated with simple filtration and recrystallization from hot ethanol.In all the cases, aromatic aldehydes substituted with either electron-donating or electron-withdrawing groups smoothly underwent the reaction and gave the target products in good to excellent yields.

In order to investigate the reusability of the prepared catalysts, the reaction of benzaldehyde, malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one was selected again as the model reaction using SPPyNs and PPyNTsAA as catalysts.After completion of the reactions, the mixtures were filtered and the recovered catalysts were washed with acetone and dried before using for next consecutive runs (2 runs). The results showed that, regarding the time and yield of the products, the sulfonated polypyrrole nanospheres catalyst has better catalytic activity than polypyrrole N-functionalized acetic acid during first to third runs but shows a slight decline in its activity during the fourth and after runs.

CONCLUSION

In conclusion, SPPyNs and PPyNTsAA catalysts were simply prepared. The prepared heterogeneous catalysts were well characterized. The

catalytic efficiency of the prepared catalysts was investigated for the preparation of 4*H*-pyrano[2,3-c]pyrazole derivatives. In the presence of the prepared solid acid catalysts, all the reactions were performed in short reaction times at high yields. It was shown that the title catalysts can be recovered and reused at least for three cycles.

ACKNOWLEDGEMENTS

We are grateful to the research council of SousangerdBranch, Islamic Azad University and Yasouj University for financial support.

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