International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.4, pp 2045-2050, 2014-2015

Sulfonatedpolypyrrole nanospheres as a green, cheap and recoverable solid acid catalyst for the synthesis of 2-amino-4*H*-chromene derivatives

Simin Nazari[1]*, Mosadegh Keshavarz[2], Shervin Saadat[3]

[1]Department of Chemistry, Sousangerd Branch, Islamic Azad University, Sousangerd 44181-6189, Iran
[2]Department of Gas and Petroleum, Yasouj University, Gachsaran, Iran
[3]Faculty of Science, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran

Abstract: Sulfonatedpolypyrrole nanospheres were synthesized by treatingpoly pyrrole nanospheres withconcentrated H_2SO_4using the ultrasonic method. The catalytic efficiency of the prepared sulfonatedpolypyrrole nanospheres for the synthesis of 2-amino-4*H*-chromene derivatives was evaluated and compared with some previously reported sulfonated solid acid catalysts. The results showed that, regarding the time and yield of the products, the present catalyst has better catalytic activity than other solid acids during first tothird runs but shows a slight decline in its activity during the fourth and after runs.
Keywords: Sulfonatedpolypyrrole nanospheres, Nano, solid catalyst, Heterogeneous, Chromene.

Introduction

The development of heterogeneous catalysts for organic synthesis has come to be a main area of research. The potential benefits of these materials over homogeneous systems such as simplified recovery, reusability and the potential for incorporation in continuous reactors and microreactors can lead to unique and environmentally benign chemical techniques for academia and industry[1].From this perspective, catalytic reactions lead to valuable processes, since the use of stoichiometric reagents that are often toxic pose essential restrictions from both an economical and an environmental standpoint and have direct relation to product purification and waste controlling[2].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[3-8].Greenchemistry not only needs the use of environmentally benign reagents and solvents, but also the recovery and reuse of the catalyst.

In this view of point, some types of solid sulfonic acid functionalized silica have been synthesized and used as an alternate to traditional homogeneous acids in catalyzing chemical transformations[9].

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[10-13]. 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[14-17]. Moreover, PPyNs can be synthesized chemically in a bulk amount from benign aqueous environment in ambient conditions, without the use of high technology and sophisticated instruments.

The 4*H*-chromene derivatives have various pharmacological properties such as anti-coagulant, anti-cancer, anti-HIV, anti-alzheimer, antitumor, diuretic, anti-malarial activities, anti-leukemic, antibacterial, anti-malarial activities, emetic, anti-anaphylactic activities and spasmolytic[18-21].

Due to the important abovementioned properties of chromene derivatives, extensive attention has been focused on the improvement of environmentally friendly methodologies to synthesize 2-amino-4*H*-chromene scaffold. The main strategy for the synthesis of chromene derivatives include the cyclization of an aromatic/ aliphatic aldehyde, malononitrile (or ethyl cyanoacetate), and diverse enolizable C-H activated acidic compound[22].Several modified methods have been reported for the synthesis of these derivatives using different homogeneous or heterogeneous catalysts such as chitosan[23], KSF[24], K_2CO_3[25] ,Na_2CO_3 under grinding[26], N,N-dimethylaminoethylbenzyldimethylammonium chloride[27],cetyltrimethylammonium chloride/bromide[28-29], tetra butyl ammonium bromide[30],triethylbenzylammonium chloride[31], nano-sized MgO[32], Mg/Al hydrotalcite[33], DBU[34], and POPINO[35]. However, many proposed methods for thesynthesis of these compounds suffer from disadvantages including relying on multi-step conditions, the use of toxic organic solvents or catalysts containing transition metals, tedious work-up procedure, troublesome waste discarding, high reaction time, and low yields. Herein, we wish to introducesulfonatedpolypyrrolenanospheres as a new and recyclable catalyst for one-pot three-component synthesis of 2-amino-4*H*-chromene derivatives in ethanol.

Experimental

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 aBruker 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 polypyrrolenanospheres (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 dodecyltrimethylammonium 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 Polyperrolenanospheres (SPPyNs)

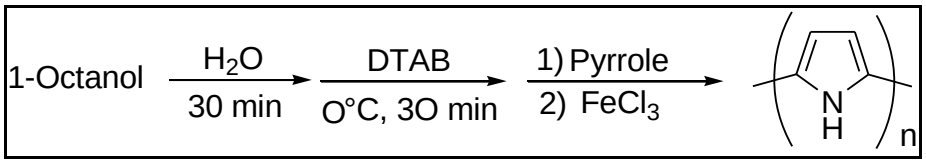
PyPNs (0.5 g) was heated in 100 ml of concentrated H_2SO_4 at 150 ◦C for 4 h. After cooling down to room temperature, ethanol (1000 ml) was added. The black solid was collected by filtration, and washed repeatedly using ethanol until no sulfate ions were detected in the filtrate [36].

2.4. General procedure for synthesis of 2-amino-4H-chromene derivatives

Enolizable compound (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), 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 2-amino-4*H*-chromene 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.[22-25]

Results and discussion

The preparation followed to obtain polypyrrole nanospheres (PPyNs) is outlined in scheme 1. Briefly, a mixture of deionized water and decyl alcohol was stirred at room temperature for 40 min. Then, dodecyltrimethylammonium bromide (DTAB) was added and after further stirring at 0 ˚C for 30 min, the emulsion was moved to an ultrasonicator. Then pyrrole was added drop-wise to the mixture. Then, $FeCl_3$ was added to initiate polymerization. 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.



Scheme 1.Preparation of PPyNs

Figure 1 shows the FESEM image of polypyrrole nanospheres (PPyNs). From figure 1, it can be seen that PPyNs have spherical shape with an average particle size of around 70-80 nm in diameter. The FESEM image of sulfonated polypyrrole 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 proposed mechanism for the preparation of SPPyNs from PPyNs has been depicted in scheme 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 catalyst recyclability of SPPNs.

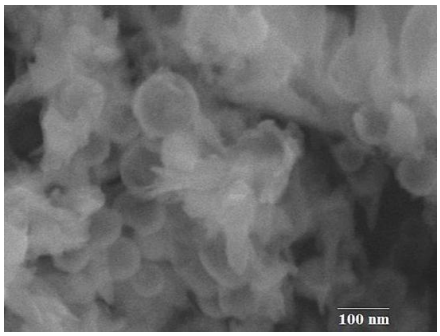


Figure 1.FESEM images of Polyperrolenanospheres (PPyNs)

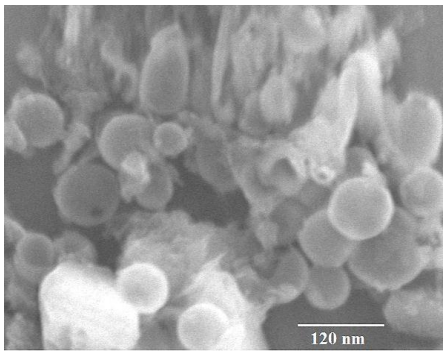
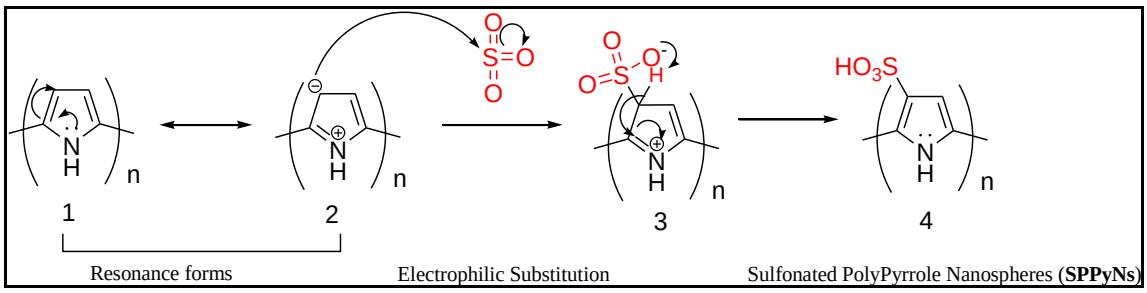


Figure 2.FESEM images of sulfonated Polyperrolenanospheres (SPPyNs)



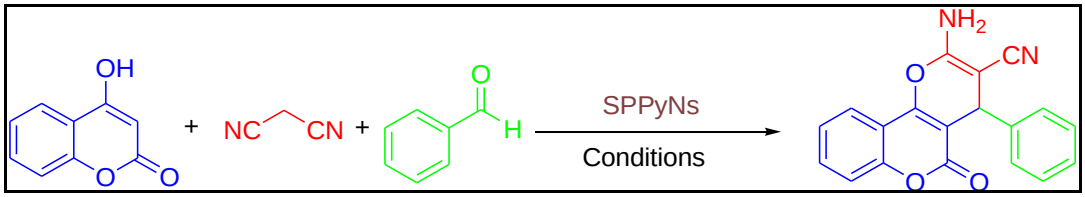
Scheme 2. Proposed mechanism of preparation of SPPyNs

On the base of our best knowledge, there is only one report that has investigated the catalytic activity of SPPyNs.[37] Herein; we became interested in investigating the catalytic activity of the prepared SPPyNs as a new heterogeneous solid acid catalyst for the synthesis of 2-amino-4*H*-chromene derivatives.

To optimize the reaction conditions, the reaction of 4-hydroxychomarine, benzaldehyde and malononitrile was selected as a model to examine the effect of SPPyNs catalyst under a variety of conditions (Table 1).

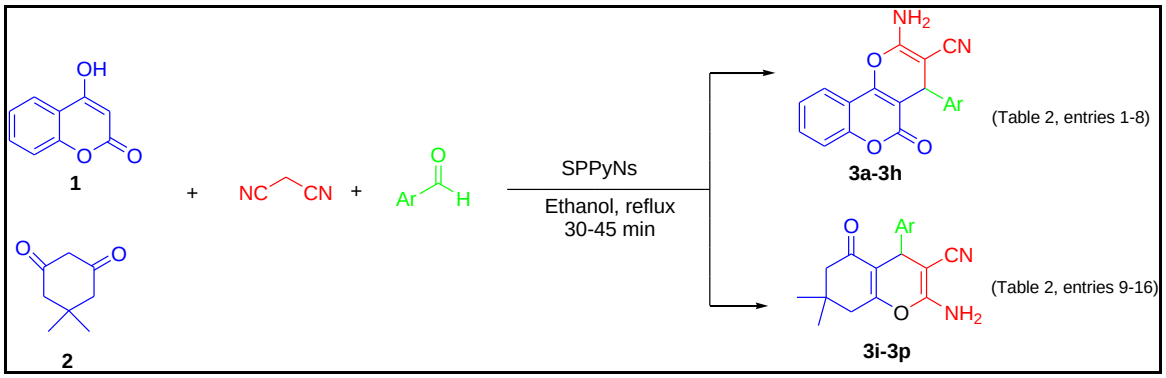
The present optimization studies revealed that the best result was achieved by caring out the reaction in the presence of 0.01 g of SPPyNs under reflux condition in ethanol (Table 1, entry 9). The larger amounts of the catalyst (0.015 g) did not improve the yield while decreasing the amount of the catalyst led to decreased yield. Using these optimized conditions, the reaction of enolizable ketones, malononitrile and various aromatic aldehydes was explored (Scheme 3).

Table 1. Investigation of catalytic activity of SPPyNs catalyst for the synthesis of 2-amino-4*H*-cromenes under various conditions



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

[a] Yield refer to isolated and pure product



Scheme 3.Synthesis of 2-amino-4*H*-chromene derivatives using SPPyNs

All the products were cleanly isolated with simple filtration and recrystallization from hot ethanol. As Table 2 shows, 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.

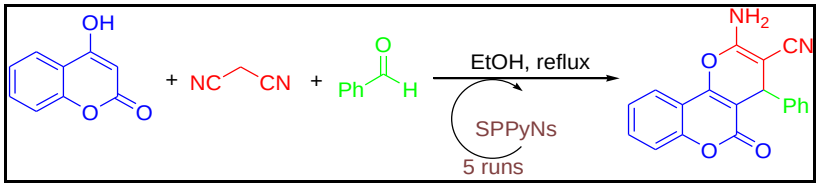
Table 2. Synthesis of 2-amino-4*H*-chromene derivatives catalyzed by SPPyNs

Entry	Enolizable compound	Ar	Product	Time (min)	Yield (%) [a]
1	**1**	C_6H_5-	**3a**	30	89
2	**1**	4-CH_3O-C_6H_4-	**3b**	35	89
3	**1**	4-CH_3-C_6H_4-	**3c**	35	85
4	**1**	2-CH_3O-C_6H_4-	**3d**	45	80
5	**1**	4-Br-C_6H_4-	**3e**	30	87
6	**1**	4-(2-methyl ethyl)-C_6H_4-	**3f**	35	85
7	**1**	4-CN-C_6H_4-	**3g**	30	90
8	**1**	3-NO_2-C_6H_4-	**3h**	30	90
9	**2**	C_6H_5-	**3i**	30	88
10	**2**	4-CH_3-C_6H_4-	**3j**	30	83
11	**2**	4-CH_3O-C_6H_4-	**3k**	30	82
12	**2**	4-Br-C_6H_4-	**3l**	30	81
13	**2**	3,4-$(CH_3O)_2$-C_6H_3-	**3m**	45	81
14	**2**	4-(2-methyl ethyl)-C_6H_4-	**3n**	40	85
15	**2**	2-CH_3O-C_6H_4-	**3o**	45	81
16	**2**	4-$N(CH_3)_2$-C_6H_4-	**3p**	35	84

[a] Yield refer to isolated and pure product

After completion of the reaction, the mixture was filtered and the recovered catalyst was washed with acetone and dried before using for next consecutive runs (4 runs). Almost consistent activity was observed over 5 consecutive runs. From table 3, it can be seen that SPPyNs catalyst can be reused up to 5 runs without need to reload and the yield difference between the first and 5th runs is 10% which indicated that the catalyst efficiency is almost maintained during 5 consecutive runs.

Table 3.Recyclability and reusability study of SPPyNs catalyst



Run	1	2	3	4	5
Time(min)	30	30	35	35	35
Yield (%)[a]	90	89	86	83	80

[a] Isolated yield.

Conclusion

In conclusion, SPPyNs were simply prepared in a straightforward single step procedure. The prepared heterogeneous catalyst was well characterized. On the base of the SEM image of the title catalyst, the size of each nanoparticle was calculated to be in the range of 60–70 nm. The catalytic efficiency of the prepared catalyst was investigated for the preparation of 2-amino-4*H*-chromene derivatives. In the presence of SPPyNs, all the reactions were performed in short reaction times at high yields. Nano size withhigh surface-to-volume ratio, Simple workup and recovery, the reusability up to 5 consecutive runs make the introduced catalyst to be a new efficient and superior catalyst for the synthesis of 2-amino-4*H*-chromene derivatives.

Acknowledgement

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

References

1. Choudhary,D.;Paul,S.;Gupta,R.;Clark,J.H. *Green Chem*. 2006, *8*, 479.
2. Ferreira,P.;Phillips,E.;Rippon,D.;Tsang,S.C. *Appl. Catal. B*,2005, *61*, 206.
3. Karimi,B.;Khalkhali, M. *J. Mol. Catal. A: Chem*.2005, *232*, 113.
4. Melero,J.A.;van Grieken, R.;Morales,G. *Chem. Rev*.2006, *106*, 3790.
5. Niknam,K.;Zolfigol, M.A.;Khorramabadi-Zad,A.;Zare, R.;Shayegh,M. *Catal. Commun.* 2006, *7*, 494.
6. Niknam,K.;Karami, B.; Zolfigol,M.A. *Catal. Commun.*2007, *8*, 1427.
7. Niknam, K.; Saberi, D.;NouriSefat, M. *Tetrahedron Lett.*2009, *50*, 4058.
8. K. Niknam, D. Saberi, M. Mohagheghnejad, *Molecules*, 2009, *14*, 1915.
9. Yoon, H.;Kim,J.;Lee, N.;Kim, B.;Jang,J. *Chembiochem*, 2008, *9*, 634.
10. Antolini, E.;Gonzalez,E.R. *Appl. Catal. A: Gen.* 2009, *365*,1.
11. Xiao,R.;Cho,S.I.I.;Liu,R.;Lee, S.B. *J. Am. Chem. Soc*.2007, *129*, 4483.
12. MalekAbbaslou, R.M.;Soltam,J.;Dalai, A.K. *Appl. Catal. A: Gen*. 2010, *379*, 129.
13. Yoon,H.;Lee, S.H.;Kwon, O.S.;Song, H.S.;Oh, E.H.;Park,T.H.;Jang,J. *Angew. Chem. Int. Ed.*2009, *48*, 2755.
14. Jang, J.;Yoon, H. *Langmuir*, 2005, *21*, 11484.
15. Wang,J.;Dai, J.;Yarlagadda,T.*Langmuir*,2005, *21*, 9.
16. Ekanayake,E.M.;Preethichandra, D.;.Kaneto, K. *Biosens. Bioelectron.*2007, *23*, 107.
17. Alvey, L.;Prado, S.;Huteau, V.;Saint-Jonis, B.;Michel, S.;Koch,M.;Cole, S.T.;Tillequin, F.;Janin,Y.L. *Bioorg. Med. Chem*. 2008, *16*, 8264.
18. Symeonidis, T.;Chamilos, M.;Hadjipavlou-Litina, D.J.;Kallitsakis, M.;Litinas, K.E. *Bioorg. Med. Lett*. 2009, *19*, 1139.
19. Kumar, D.;Reddy, V.B.;Sharad, S.; Dube, U.;Kapur, S.*Eur. J. Med. Chem*. 2009, *44*,3805.
20. Alvey, L.;Prado,S.;Saint-Joanis, B.;Michel, S.;Koch, M.;Cole, S.T.;Tillequin,F.;Janin, Y.L. *Eur. J. Med. Chem*. 2009, *44*, 2497.
21. Ballini, R.;Bosica, G.;Conforti, L.M.;Maggi, R.;Mazzacani, A.;Righi, P.;Sartori, G. *Tetrahedron*, 2001, *57*, 1395.
22. Al-Matar, M.;Khalil, K.D.;Meier, H.;Kolshorn, H.; Elnagdi, M.H. *Arkivoc*2008, xvi, 288.
23. Ballini, R.;Bigi, F.;Conforti, M.L.;Santis, D.D.;Maggi, R.;Oppici, G.;Sartori, G. *Catal. Today*.2000, *60*, 305.
24. Kidwai, M.;Saxena, S.;Rahman Khan, M.K.;Thukral, S.S. *Bioorg. Med. Chem. Lett.*2005, *15*, 4295.
25. Naimi-jamal, M.R.;Mashkouri,S.;Sharifi,A. *Mol. Divers*. 2010, *14*, 473.
26. Lu, C.;Huang, X.J.;Li, Y.Q.;Zhou, M.Y.;Zheng, W. *Monatsh. Chem*. 2009, *140*, 45.
27. Jin, T.S.;Xiao, J.C.;Wang, S.J.;Li, T.S. *Ultrason. Sonochem*.2004, *11*, 393.
28. Jin, T.S.;Zhang, J.S.;Liu, L.B.;Wang, A.Q.;Li, T.S.*Synth. Commun*.2006, *36*, 2009.
29. Jin, T.S.;Xiao, J.C.;Wang, S.J.;Li, T.S.;Song,X.R. *Synlett*,2003,2001.
30. Shi, D.Q.;Zhang, S.I.;Zhuang,Q.Y.; Wang, X.S. *Chin. J. Org. Chem*. 2003, *23*, 1419.
31. Kumar,D.;Reddy, V.B.;Mishra, G.B.;Rann, R.K.;Nadagouda, M. N.;Varma, R.S. *Tetrahedron*,2007, *63*, 3093.
32. Surpur, M.P.;Kshirsagar, S.;Samant, S. *Tetrahedron Lett.*2009, *50*, 719.
33. Khurana, M.J.;Nand, B.;Saluja, P. *Tetrahedron*, 2010, *66*, 5637.
34. Dekamin, M.G.;Eslami, M.;Maleki, A. *Tetrahedron*, 2013, *69*,1074.
35. Tian,X.;Sub F.; and Zhao, X. S. *Green Chem.*, 2008, *10*, 951.

*****