Nickel ferrite as a recyclable nanocatalyst for synthesis of novel highly substituted 1,4-dihydropyrano[2,3-c]pyrazole derivatives

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Abstract

Highly substituted 1,4-dihydropyrano[2,3-c]pyrazole derivatives were synthesized by four-component reaction of aromatic aldehydes, malononitrile, ethyl acetoacetate and various phenylhydrazine, using nickel ferrite as a recyclable nanocatalyst by a grinding method under solvent-free and thermal conditions. The reaction has the advantages of good yields, less pollution, ease of separation of the desired products, and being environment-friendly. A possible mechanism for this reaction was proposed.

Keywords: 1,4-Dihydropyrano[2,3-c]pyrazoles; one-pot synthesis; four component reaction; nickel-ferrite nanoparticles nanocatalyst.

Introduction

In recent years, the synthesis of $4H$-pyran has attracted considerable interest as an important intermediate of many heterocycles [1,2]. This type of compound exhibits attractive pharmacological and biological properties as antiallergic [3] and antitumor agents [4,5]. The $4H$-pyran ring can be transformed to pyridine systems, which relate to pharmacologically important calcium antagonists of the DHP type [6]. Recently, a few reports have described the synthesis of substituted pyrano[2,3-c]pyrazole derivatives *via* MCRs of aldehyde, malononitrile, and 3-methyl-2pyrazoline-5-one in organic solvent (i.e. ethanol or DMF) using piperidine [7], KF.2H$_2$O, triethylamine [8], triethylbenzylammonium chloride (TEBA) [9] and D,L-Proline [10], but

most of them are toxic. The need to reduce the amount of toxic waste and by-products arising from chemical processes requires increasing emphasis on the use of less toxic and environmentally compatible materials in the design of new synthetic methods. A move away from the use of solvents in organic synthesis has led in some cases to improved results and milder synthetic procedures, and the solvent-free thermal reactions are more important for practical synthetic processes industry [11]. In the last few years, application of this nanocatalyst in organic and inorganic reactions has emerged as a rapidly growing field. ZnO nanoparticles applied as an efficient catalyst for the one-pot synthesis of α-amino phosphonates [12], synthesis of β-acetamido ketones/esters using ZnO nanoparticles

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[13], aerobic oxidative processes by supported gold nanoparticles [14], etc. As part of our current study in the development of new synthetic methods in heterocyclic chemistry and our nearest in pyrazole-based MCRs, herein we describe an efficient synthesis of substituted pyrano[2,3-c]pyrazols *via* a four-component reaction catalyzed by $NiFe_2O_4$ magnetic nanoparticles under solvent-free, thermal conditions (Scheme 1).
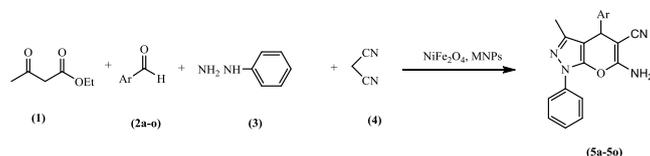
Ar: C_6H_5, 4-$CH_3C_6H_4$, 4-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 2,4-$Cl_2C_6H_4$, 4-FC_6H_4, 4-BrC_6H_4, 4-OHC_6H_4, 4-$OCH_3C_6H_4$, 2,4-$(OCH_3)_2C_6H_3$, 4-CNC_6H_4, 3-Pyridyl

Scheme 1. Four-component synthesis of substituted pyrano[2,3-c]pyrazole drivatives

Experimental

Materials and instrumentation

The entire chemicals used were of synthesis grade reagents (Merck) and used as received. The morphology of catalysts and their precursors were observed by means of a Philips XL30 scanning electron microscopy (SEM). Mass spectra were recorded on a VG micromass 7070H and Finnigan mat 1020B mass spectrometers operating at 70 eV. Elemental analyses were performed on Yanco-CHN CORDER elementary analyzer. The IR spectra of the samples (as KBr pellets) were recorded using a Rayleigh WQF-510 spectrophotometer in the range of 400-4000 cm^{-1}. Melting points were determined using Barnstead-Electro thermal 9300 Melting Points. ^{1}H NMR spectra were recorded on Bruker 500 MHz NMR spectrometer.

Preparation of Ni-Ferrite oxide magnetic nano catalyst

In a typical reaction, stoichiometric amounts of $Fe(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ were dissolved in deionized water. The *p*H of the solution was subjected to 9 by addition of aqueous ammonia, and then the solution was stirred vigorously for 15 h at 80 °C and the precipitate so appeared was filtered, washed, and dried. Thus, the composite hydroxide metals so formed is calcinated at 550 °C for 5 h. After calcination, $Ni_xFe_{1-x}O4$ (magnetic nano Ni-Ferrite oxide) is formed. The catalyst materials were synthesized by varying composition of Ni (II) and Fe (III) such as

(a) x=0.8, (b) x=0.6, (c) x=0.4, (d) x=0.2

General procedure for the synthesis of 6-amino-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile using nickel ferrite oxide magnetic nano catalyst

A mixture of phenyl hydrazine **3** (1 mmol), ethyl acetoacetate **1** (1 mmol) was stirred at 0 °C until 3-methyl-2-pyrazoline-5-one was precipitated and its formation was completed (10 min). The reaction was then left to warm to room temperature. Benzaldehyde **2a** (1 mmol), malononitrile **4** (1 mmol) and nickel ferrite magnetic nano catalyst (0.1 g) were then added and the mixture was heated to 125 °C or 100 °C for the appropriate time (Table 4), respectively. The progress of reaction was monitored by TLC. After the completion of reaction, 10 mL ice cold water was added to the reaction mixture. To get the pure product, the

solid obtained was filtered and recrystallized from ethanol.

Spectral data of products

6-Amino-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

(5a)

0.314 g (96%), White solid, mp: 166-168 °C. IR (KBr): 3329, 3320, 3154, 2231, 1643, 1610, 1542, 1434, 1132, 1054, 1021, 782, 743, 756 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): δ= 1.81 (s, 3H), 4.73 (s, 1H), 7.32 (s, NH$_2$, 2H), 7.37-7.45 (m, 3H, Ar-H), 7.48-7.56 (m, 3H, Ar-H), 7.59 (t, *J*=8 Hz, 2H, Ar-H), 7.87 (d, *J*=8 Hz, 2H, Ar-H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ= 12.8, 37.8, 58.0, 98.6, 109.6, 119.6, 126.9, 128.1, 128.9, 129.3, 129.9, 138.9, 144.8, 146.7, 159.8, 182.7. MS (EI), m/z (%) =328 (M+, 65), 251 (25). Anal Calcd for C$_{20}$H$_{16}$N$_4$O: C, 73.15; H, 4.91; N, 17.06. Found: C, 73.19; H, 4.95; N, 17.02.

6-Amino-3-methyl-4-(naphthalen-2-yl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5n)

0.340 g (90%), white solid, mp: 205-207 °C. IR (KBr): 3415, 33212, 3067, 2232, 1633, 1611, 1553, 1476, 1411, 1154, 1011, 754, 645, 632 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): δ= 1.64 (s, 3H), 5.41 (s, 1H), 6.93 (s, 1H), 7.39-7.54 (m, 4H), 7.89 (d, J=8.1 Hz, 2H), 7.98 (d, J=8.1 Hz, 2H), 8.01-8.15 (m, 3H, Ar-H), 8.01 (8.3 (brs. 2H, NH$_2$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ=12.1, 27.3, 59.1, 119.3, 121.5, 122.7, 126.8, 127.9, 128.9, 129.1, 129.9, 130.2, 131.6, 140.1, 141.5, 142.6, 145.1, 157.1, 179.9. MS (EI), m/z (%) =378 (M+, 58), 250 (35). Anal Calcd for C$_{24}$H$_{18}$N$_4$O: C, 76.17; H, 4.79; N, 14.81. Found: C, 76.19; H, 4.76; N, 14.83.

6-Amino-3-methyl-1-phenyl-4-(pyridin-4-yl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5o)

0.299 g (91%), white solid, mp: 195-197 °C. IR (KBr): 3421, 3326, 3052, 2187, 1654, 1601, 1583, 1489, 1421, 1143, 1065, 764, 676, 612 cm^{-1}. ^{1}H NMR (DMSO-d_6, 500 MHz): δ= 1.82 (s, 3H), 4.64 (s, 1H), 7.01 (t, *J*=6.4, 1H), 7.40 (S, 2H, NH$_2$), 7.53 (t, *J*=7.6 Hz, 2H), 7.61 (d, *J*=8.7 Hz, 2H), 7.85 (d, *J*=8.4 Hz, 2H), 8.23 (d, *J*=8.8 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ= 10.8, 37.4, 57.8, 96.8, 121.7, 123.5, 127.9, 128.9, 132.8, 134.8, 136.8, 151.8, 153.8, 156.8, 161.8. MS (EI), m/z (%) =329 (M+, 70), 250 (45). Anal Calcd for C$_{19}$H$_{15}$N$_5$O: C, 69.29; H, 4.59; N, 21.26. Found: C, 69.30; H, 4.61; N, 21.27.

Results and discussion

To compare the applicability and efficiency of our catalyst with catalyst reported for the synthesis of 1,4-dihydropyrano[2,3-c]pyrazole, we have tabulated results for these catalysts (Table 1). As it is apparent from Table 1, NiFe$_2$O$_4$ magnetic nanoparticles remarkably improved the synthesis of 1,4-dihydropyrano[2,3-c]pyrazoles in terms of reaction time and yield (Table 1, Entry 11).

Table 1. Comparison of results for $NiFe_2O_4$ magnetic nanoparticles catalysts with those for other catalysts reported in the literature for preparation of 1,4-dihydropyrano[2,3-c]pyrazole derivatives

Entry	Catalyst	Conditions	Time (min)	Yield (%)[a]	Ref.
1	Et_3N	EtOH, Reflux	10	80	[15]
2	L-Proline (5 mol%)	H_2O, Reflux	10	90	[16]
3	L-Proline (5 mol%)	EtOH, Reflux	10	87	[16]
4	γ-Alumina (15 mol%)	H_2O, 100 °C	50	80	[16]
5	KF-alimina (5 mol%)	EtOH, Reflux	12	80	[16]
6	Trichloroacetic acid (10 mol%)	Solvent free, 100 °C	5	85	[17]
7	Maltose (20 mol%)	Solvent free, 100 °C	10	98	[18]
8	$Ce(SO_4)_2$ (10 mol%)	Solvent free, 100 °C	5	80	[18]
8	Imidazole (50 mol%)	H_2O, 80 °C	20	89	[15]
9	H_3PO_4/Al_2O_3 (0.08 mol%)	Solvent free, 100 °C	7	97	[19]
10	Triethylbenzylammonium chloride (TEBA)	H_2O, 90 °C	360	99	[20]
11	$NiFe_2O_4$ nanoparticles	Solvent free, 125 °C	5	96	Present work

[a]Isolated yield

The effect of temperature on the rate of reaction was studied at different temperatures for the preparation of 6-amino-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile using for $NiFe_2O_4$ magnetic nanoparticles catalysts under thermal, solvent free conditions. It was observed that the reaction did not proceed at room temperature. At 60 °C, the reaction proceeded smoothly and almost the complete conversion of the product was observed. Further increase in temperature at 100, 110, 12 and 130 °C increased the rate of reaction. Therefore, we kept the reaction at 125 °C (giving short reaction time and high yield).

To find the optimized amount of nickel ferrite magnetic nano catalyst as shown in (Table 2), the reaction was carried out varying the amount of the catalyst on the conversion of 1,4-dihydropyrano[2,3-c]pyrazoles using for $NiFe_2O_4$ magnetic nanoparticles.

The conversion of 6-amino-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile increased linearly with the catalyst weight up to 100 mg nickel ferrite oxide magnetic nano catalyst and then becoming constant. These results indicate that the amount of magnetic nano catalyst is required for the conversions.

Table 2. Optimization of the amount of catalyst for synthesis of of 6-amino-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile using NiFe$_2$O$_4$ magnetic nanoparticles

Entry	Catalyst (mg)	Time (min)	Yields (%)[a]
1	-	30	-
2	10	20	30
3	30	25	45
4	50	20	57
5	70	15	65
6	90	10	70
7	100	5	96
8	110	5	96
9	120	5	94

[a]Isolated yield

By the use of these optimized reaction conditions, the scope and efficiency of the reaction were investigated for the synthesis of a wide variety of substituted 1,4-dihydropyrano[2,3-c]pyrazoles using phenyl hydrazine or 2,4-dinitrophenyl hydrazine, ethyl acetoacetate, arylaldehydes, and malononitrile. The results are summarized in Table 3. Interestingly, a variety of aryl aldehydes including those with electron withdrawing or releasing substituents (*ortho*, *meta*, *para*-substituted) participated well in this reaction and gave the 1,4-dihydropyrano[2,3-c]pyrazole drivatives in good to excellent yield.

Table 3. Four-component synthesis of 1,4-dihydropyrano[2,3-c]pyrazole derivatives[a]

Entry	Ar	Time (min)	Yields (%)[b]	M.P. (ºC)	
				Found	Lit. [Ref.]
1	C$_6$H$_5$	5	96	167-169	166-168 [16, 17]
2	4-CH$_3$C$_6$H$_4$	10	93	175-177	176-178 [16, 17]
3	4-NO$_2$C$_6$H$_4$	5	98	192-194	191-193 [16, 17]
4	3-NO$_2$C$_6$H$_4$	5	98	189-191	190-191 [16, 17]
5	2-ClC$_6$H$_4$	5	97	145-147	144-146 [16, 17]
6	3-ClC$_6$H$_4$	5	95	159-161	158-159 [16, 17]
7	4-ClC$_6$H$_4$	5	96	171-173	174-175 [16, 17]
8	2,4-Cl$_2$C$_6$H$_3$	5	96	184-186	182-184 [16, 17]
9	4-FC$_6$H$_4$	5	98	168-170	167-169 [16, 17]

10	4-BrC$_6$H$_4$	5	94	181-183	183-184 [16, 17]
11	4-OHC$_6$H$_4$	10	88	210-212	211-212 [16, 17]
12	4-CH$_3$OC$_6$H$_4$	5	95	171-173	170-172 [16, 17]
13	2,4-(CH$_3$O)C$_6$H$_3$	5	95	177-179	176-178 [16, 17]
15	2-Naphthyl	15	90	205-207	New compound
14	4-Pyridinyl	10	91	196-198	195-197[24-27]

[a]Reaction conditions: phenyl hydrazine: ethyl acetoacetate: arylaldehyde: malononitrile (1:1:1:1, molar ratio); Solvent: free; Catalyst: nickel ferrite nano; Catalyst amt: 100 mg.
[b]Isolated yield

In accordance with the literature [21], we proposed a mechanism for synthesis of 1,4-dihydropyrano[2,3-c]pyrazoles in the presence of NiFe$_2$O$_4$ magnetic nanoparticles as catalyst. First, pyrazolone (**III**) was formed by reaction of (**1**) and (**3**). Knoevenagel condensation between (**2a-o**) and (**4**) produced 2-benzylidenemalononitrile (**6**). Michael addition of (**IV**) and (**V**), followed by cyclization and tautomerization afforded the corresponding product (**5a-o**) (Scheme 2).
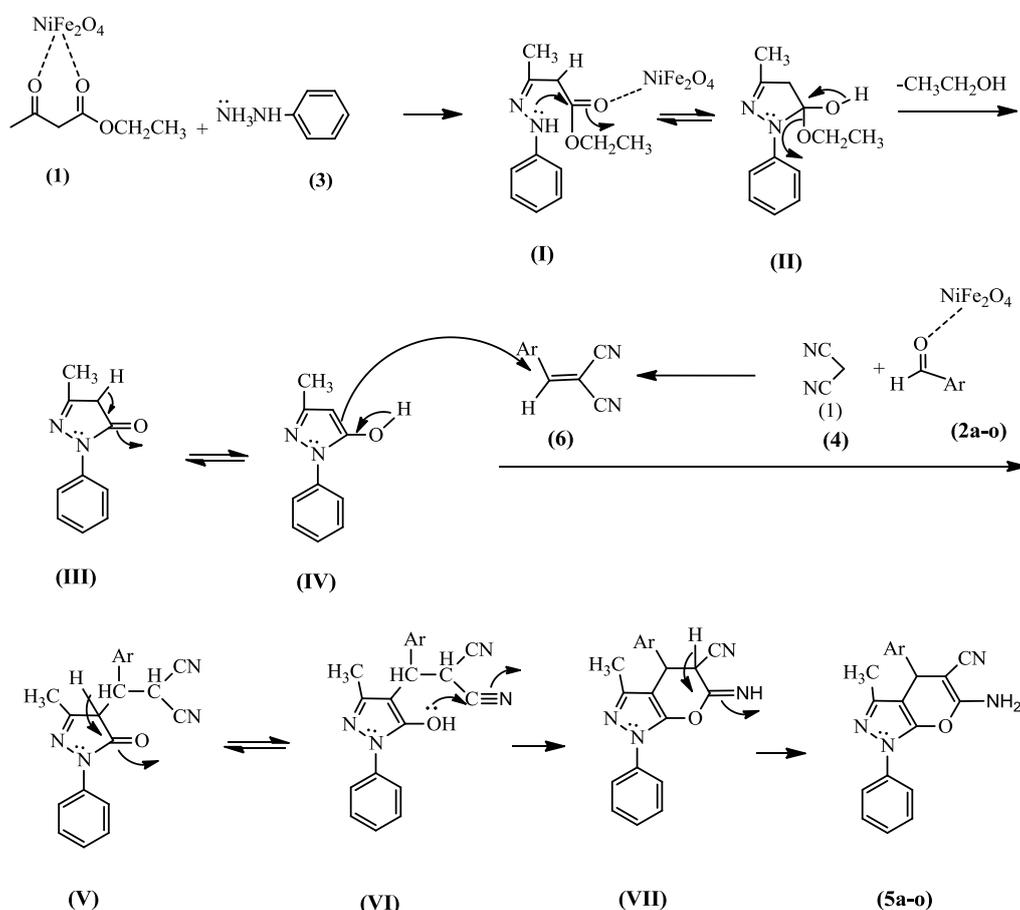

Scheme 2. Proposed mechanism for the formation of 1,4-dihydropyrano[2,3-c]pyrazole derivatives

The range of [Ni]/[Fe] solution ratios varied from 80% Ni to 80% Fe and the catalytic performance for the synthesis of 6-amino-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile was studied. The catalytic conversion as well as the yield for 6-amino-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile increased with increasing the concentration of Fe. However, maximum yield (96%) of 6-amino-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-

c]pyrazole-5-carbonitrile was achieved with ratios [Ni]/[Fe]=0.4.

The synthesized $Ni_xFe_{1-x}O_4$ magnetic nanoparticles catalyst: (a) x=0.8, (b) x=0.6, (c) x=0.4, (d) x=0.2 showed the crystal structure of magnetic nanoparticles. The surface morphology of the synthesized Ni-Ferrite is studied by scanning electron micrograph and are shown in Figure 1.

The SEM micrograph of Ni-Ferrite magnetic nanocatalyst shows agglomeration of particles and irregularity in shape. The prepared samples have spongy and fragile network structure with voids and pores.
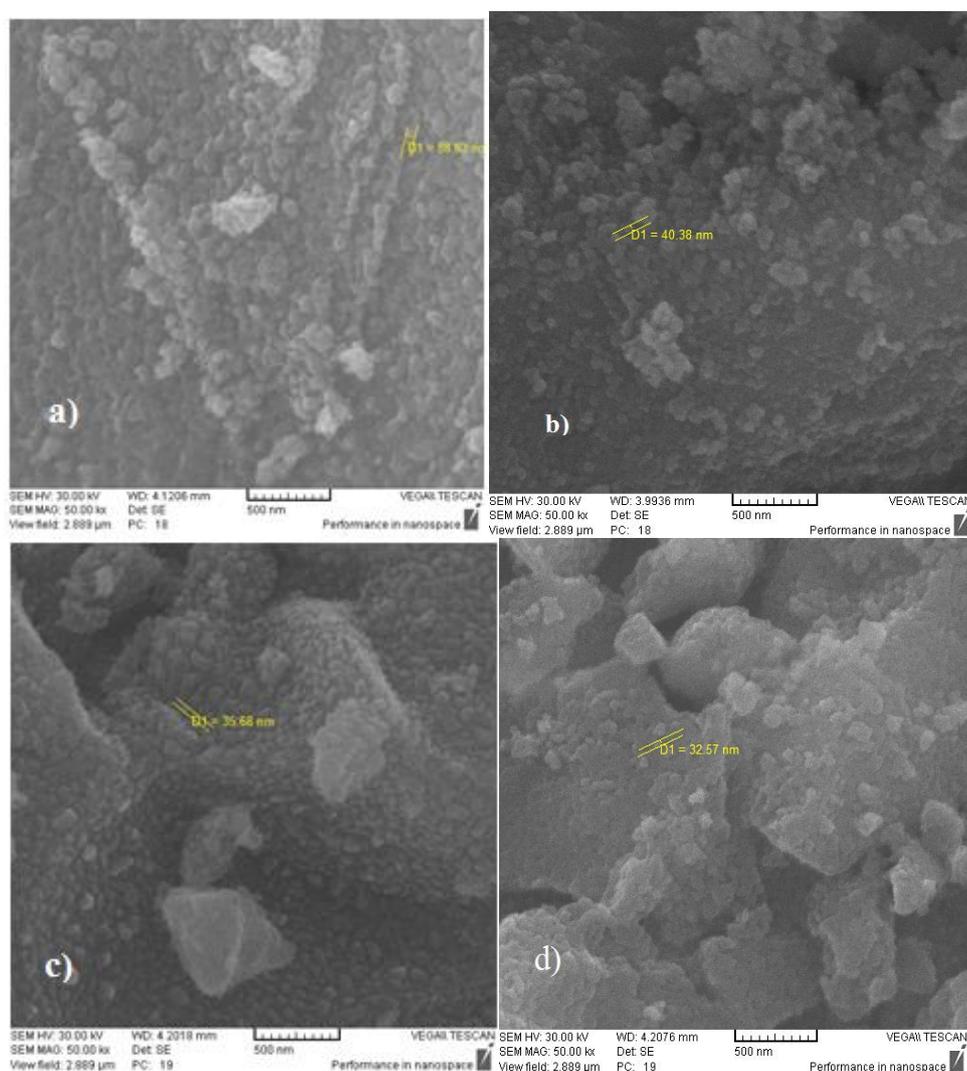
Figure 1. SEM image for the morphology of the $Ni_xFe_{1-x}O_4$ magnetic nanoparticles catalyst: (a) x=0.2, (b) 0.4, (c) x=0.6, (d) x=0.8

From the data obtained by SEM micrographs, the particle size histograms can be drawn and the mean size of the particles can be determined. Figure 2 shows the particle size distribution of $Ni_xFe_{1-x}O_4$ (x=0.2-0.8) magnetic nanoparticles. It can be seen that the particle sizes possess a small and narrow size distribution in a range from 60 to 90 nm, and the maximum frequency- particle diameter is x=0.8. We notice that the mean particle size determined by SEM is in good agreement with the average crystallite size calculated by the Scherer formula from the XRD patterns. According to the SEM image, it could be concluded that this preparation method had successfully overcome the problem of agglomeration and route of appropriate to obtain the $Ni_xFe_{1-x}O_4$ magnetic magnetic nanoparticles (x=0.8) with smaller crystalline size.
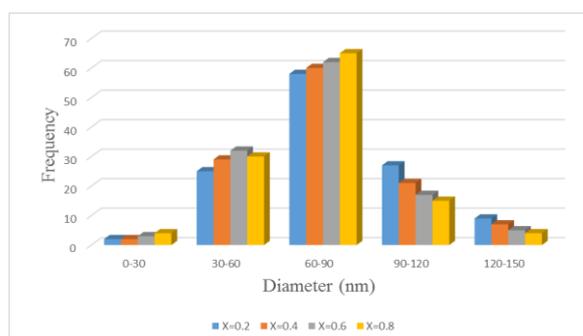
Figure 2. Particle size distribution of the $Ni_xFe_{1-x}O_4$ magnetic nanoparticles catalyst: (a) x=0.2, (b) x=0.4, (c) x=0.6, (d) x=0.8

Also, the crystallite size of the samples is estimated from the broadening of the XRD peaks using the Scherrer formula [22].

$$D=0.9\lambda/\beta\cos\theta$$

Where D is crystallite size, β is full width at half maximum (FWHM) of the (41.72) 2Theta peak, λ is X-ray wavelength and θ is diffraction angle. Average crystallite size for all samples was obtained in Table 4. The crystallite size was found to be increasing with decreasing substitution of nickel ions. This is due to the fact that the radius of Ni ions is smaller than that of Fe ions (Figure 3).

Table 4. Crystallite size (nm) of synthesized samples

Entry	x	D(nm)
1	0.8	36.87
2	0.6	39.09
3	0.4	41.78
4	0.2	59.89
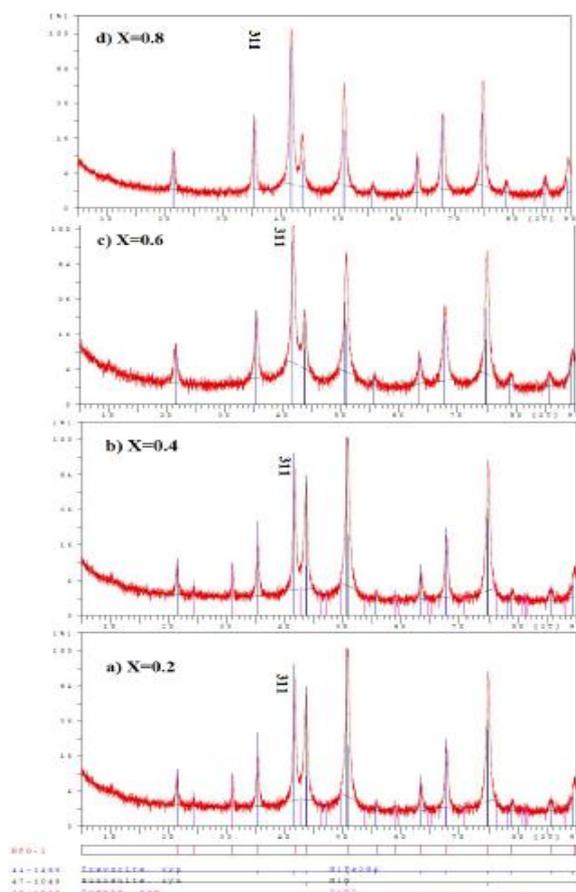
Figure 3. XRD Pattern of NiFe$_2$O$_4$ magnetic nanoparticles where, (a) x=0.2, (b) x=0.4, (c) x=0.6, (d) x=0.8 at 550 ^{o}C

The re-use of nickel ferrite magnetic nanoparticles (x=0.4) was investigated in the reaction methylacetoacetate (1), 4-chlorobenzaldehyde (2g), phenyl hydrazine (3) and malononitrile (4). After the completion of the reaction, the products together with the catalyst were precipitated out. The catalyst was separated, by putting external magnet, from the precipitate by adding ethanol which dissolved the organic compound. The catalyst was washed with ethyl acetate, dried at 110 ^{o}C and subjected to fresh reaction. The catalyst was found to be reusable five times without significant loss of activity.

FT-IR spectrum of the nickel ferrite magnetic nanocatalyst shows that the broad absorption band centered at 3410 cm^{-1} is attributable to the band O–H stretching vibrations and the weak band near 1623 cm^{-1} is assigned to H–O–H bending vibrations mode which were also presented due to the adsorption of water in air when FT-IR sample disks were prepared in an open air. A peak observed at 604 cm-1 indicates the Ni-O cm^{-1} [23].

Conclusion

In summary, we have developed a new method for the synthesis of 1,4-dihydropyrano[2,3-c]pyrazole derivatives from phenyl and 2,4-dinitrophenyl hydrazine 3, ethyl acetoacetate 1, arylaldehyde 2a-o and malononitrile 4 using NiFe$_2$O$_4$ magnetic nanoparticles catalyst. Our method has several advantages

including short reaction times, mild conditions, excellent yields, inexpensive and non-toxic catalyst, simple operation and work-up. Additionally, the protocol does not require volatile and hazardous organic solvents and an additional ultrasound or microwave oven. The elimination of the solvent has obvious environmental benefits with regard to the depletion of solvent waste. Also, the catalyst could be successfully recovered and recycled at least for five runs without significant loss in activity.

Acknowledgments

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