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Co_3O_4 nanoparticles as a robust and recoverable catalyst for one-pot synthesis of polyhydroquinolines and tetrahydrobenzopyrans

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ABSTRACT

This study introduces a green and efficient method for preparation of biologically-active substituted 4H-pyrans using the one-pot three-component reaction of aromatic aldehydes, dimedone and malononitrile in the presence of cobalt oxide nanoparticles. Co_3O_4 nanoparticles were used as an efficient catalyst for the synthesis of polyhydroquinoline derivatives by the reaction of aromatic aldehydes, ethyl acetoacetate, dimedone and ammonium acetate. The preparation and use of Co_3O_4 as a powerful and reusable nanocatalyst under solvent-free conditions is described. The catalyst was characterized by spectral techniques including XRD, FE-SEM, FT-IR, VSM, EDX and TEM analysis. This method offers the advantages of high yield, short reaction time, comfortable work-up and reusability of the catalyst.

***Keywords**: One-pot, Nanocatalyst, Tetrahydrobenzopyran, Polyhydroquinoline, Solvent-free, Co_3O_4.*

1. Introduction

Tetrahydrobenzo[*b*]pyran and polyhydroquinoline derivatives have attracted substantial attention for their anticoagulant [1], anticancer [2], cytotoxic [3], diuretic [4], anti-anaphylactin [5], anti-tumor [6] and anti-HIV [7] properties.

The 1,4-dihydropyridine nucleus of quinolines are bioactive compounds that are well-known analogues of NADH coenzymes [8], Ca^{2+} channel-blockers [9] and cardiovascular agents [10]. Substituted 4H-pyrans are considered to be anti-cancer agents [11] and are core to the structure of several natural products [12].They can be employed as operator for treatment of neurodegenerative diseases such as Alzheimer's [13] and Parkinson's [14] diseases and schizophrenia [15].

Industrial and synthetic roles of 4H-pyranes and polyhydroquinolines include electrolysis [16], solar thermal energy [17], metal triflates [18], Ru (II) complexes [19], Ni nanoparticles [20], ionic liquid [21] and silica gel [22], have been reported for the synthesis of these compounds. Interest in a combination of Co_3O_4 and carbon nanotubes (CNTs) has increased owing to their wide applications [23,24].

Each method has its own competency, but some require expensive catalysts, have poor yield, harsh reaction conditions, difficult work-ups and long reaction times.

The search for methods of synthesis of these compounds using multi-component reactions (MCRs) under mild conditions is ongoing.

Multi-component reactions are synthetically beneficial organic reactions in which three or more substrates react together to provide a final product [25]. Nanocatalysts have been used to increase the efficiency and performance of multicomponent reactions. Nanoparticles have high surface-to-volume proportion and coordination sites, which enables many active sites [26]. Recent attempts have been directed to the synthesis of Co_3O_4 nanoparticles. Co_3O_4 is a significant, antiferromagnetic p-type semi-conductor that offers gas-sensing, catalytic and electrochemical properties [27-29]. These nanoparticles have fundamental applications in elecrochromic devices, lithium batteries, solid-state sensors and catalysis [30-33].

The present study introduces Co_3O_4 nanoparticle as an efficient catalyst for the synthesis of 4H-pyran and polyhydroquinoline derivatives using one-pot three/four-component reactions under solvent-free conditions (Scheme 1).

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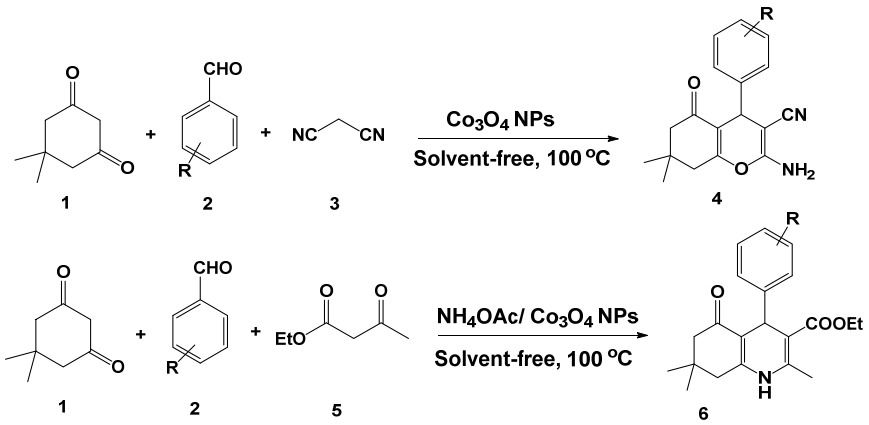


Scheme 1. One-pot synthesis of polyhydroquinolines and tetrahydrobenzopyrans catalyzed by Co_3O_4 nanoparticles.

2. Experimental

Chemicals were purchased from the Sigma-Aldrich and Merck in high purity. All of the materials were of commercial reagent grade and were used without further purification. All melting points were uncorrected and determined by the capillary tube on Boetius melting point microscope. ^{1}HNMR and ^{13}CNMR spectra were obtained on a Bruker 400 MHz spectrometer with $CDCl_3$ as solvent using TMS as an internal standard. FT-IR spectrum was recorded on Magna-IR, spectrometer 550. The elemental analyses (C, H, N) performed by a Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with mono chromatized Cu Kα radiation (λ = 1.5406 Å). Microscopic morphology of products was visualized by SEM (LEO 1455VP). The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV. Magnetic properties were obtained by a BHV-55 vibrating sample magnetometer (VSM) Transmission electron microscopy (TEM) was performed with a Jeol JEM-2100UHR, operated at 200 kV. made by MDK-I.R.Iran. compositional analysis was done by energy dispersive analysis of X-ray (EDX, Kevex, Delta Class I).

2.1. Preparation of Co_3O_4 nanoparticles

Co_3O_4 MNPs were prepared according to previously reported procedure by Vela et. al with some modifications [32]. Firstly, cobalt nitrate hexahydrate (8.60 g) was dissolved in 100 ml of ethanol and the resulting mixture was vigorously stirred. Then, the mixture was heated to 50ºC and kept for 30 min. finally oxalic acid (2.14 g) was added quickly to the solution and the reaction mixture was stirred for 2 h at 50°C. The formed precipitate including cobalt (II) oxalate was collected by centrifuges and then the prepared cobalt (II) oxalate powder was calcined at 400ºC for 2 h to produce Co_3O_4 nanoparticles.

2.2. General procedure for the preparation of synthesis of tetrahydrobenzopyran derivatives

A mixture of aldehyde (1 mmol), dimedone (1 mmol), malononitrile (1mmol) and Co_3O_4 NPs 0.02 g (10% mol) was added to a round bottom flask with stirring in the oil bath at 100ºC for suitable times. Upon completion as monitored by TLC, the reaction mixture was cooled and dissolved in chloroform. The catalyst was insoluble in $CHCl_3$ and separated by a magnet. Finally the pure product was obtained by evaporation of the solvent under reduced pressure.

2.3. General procedure for the preparation of polyhydroquinoline derivatives

Co_3O_4 NPs 0.02 g (10% mol) was added to a mixture of 5,5-dimethyl-1,3-cyclohexanedione (0.14 g, 1 mmol), various aldehydes (1 mmol), ammonium acetate (1 mmol) and ethyl acetoacetate (1 mmol) and then the mixture was heated at 100ºC for 40-70 min. Evolution of the reaction was constantly monitored by TLC. After end of the reaction, the mixture was dissolved in dichloromethane andcontinued by separation of the catalyst. The solvent was separated under vacuum and the pure polyhydroquinolines were obtained by recrystallization from ethanol.

All of the products were characterized and identified with m.p., ^{1}HNMR, ^{13}CNMR and FT-IR spectroscopy techniques.

Spectral data for new compounds

*2-amino-7,7-dimethyl-4-(4-(methylthio)phenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4b**):*

White solid. m.p.= 217-218°C; FT-IR (KBr): $\bar{\nu}$ = 3446 (NH_2), 3328 (NH_2), 2978, 2210 (CN), 1678 (CO),

1528, 1334, 1229(C-O) cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.12-2.23 (m, 4H, 2×CH_2), 2.31 (s, 3H, SCH_3), 5.09 (s, 1H, CH), 6.24 (bs, 1H, NH_2), 6.98-7.01 (d, *J* =7.8 Hz, 2H, ArH), 7.29-7.31 (d, *J* = 7.8 Hz, 2H, ArH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ = 18.8, 25.1, 26.2, 33.1, 34.9, 44.9, 48.2, 57.9, 110.1, 119.3, 123.6, 130.1, 145.4, 155.1, 157.8, 163.5, 194.7 ppm. MS (EI): m/z= 340.44 (M^+). Anal. Calcd. For $C_{19}H_{20}N_2O_2S$: C 67.03, H 5.92, N 8.23; Found: C 67.13, H 5.82, N 8.16 %.

2-amino-4-(2,3-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(4J)****:*

White solid. m.p.= 168-170°C. FT-IR (KBr): $\bar{\nu}$ = 3435 (NH_2), 3297 (NH_2), 2964, 2206 (CN), 1682 (CO), 1544, 1341, 1217 (C-O) cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 0.99 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 2.04-2.15 (m, 4H, 2×CH_2), 3.71 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 5.12 (s, 1H, CH), 6.33 (bs, 1H, NH_2), 6.93-7.21 (m, 3H, ArH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ = 25.3, 26.7, 34.4, 35.8, 43.7, 49.1, 53.2, 55.4, 57.9, 109.2, 118.6, 122.9, 131.4, 136.7, 138, 9, 145.2, 1545, 157.6, 163.2, 195.1. MS (EI): m/z= 340.44 (M^+). Anal. Calcd. For $C_{20}H_{22}N_2O_4$: C 67.78, H 6.26, N 7.90; Found: C 67.63, H 6.37, N 8.02 %.

2-(3-(ethoxycarbonyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinolin-4-yl)benzoic acid ***(6i)****:*

White solid (recrystallized from ethanol). m.p. = 231-232ºC. FT-IR (KBr): $\bar{\nu}$ = 2543-3522 (COOH), 3314 (NH), 1708 (C=O), 1683 (C=O), 1662, 1525, 1346, 1221 (C-O) cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 0.97 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.31 (t, 3H, $OCH_2C\underline{H}_3$), 2.08 (s, 3H, CH_3), 2.14-2.21 (m, 4H, 2×CH_2), 3.98 (q, 2H, $OC\underline{H}_2CH_3$), 5.23 (s, 1H, CH), 6.54 (s, 1H, NH), 7.18-7.82 (m, 4H, Ar-H), 11.89 (bs, 1H, COOH) ppm. ^{13}CNMR (100 MHz, $CDCl_3$): δ = 14.8, 21.3, 25.5, 31.4, 33.7, 42.1, 45.7, 48.3, 58.8, 105.9, 124.3, 126.1, 129.8, 133.4, 141.2, 144.1, 147.6, 150.9, 166.1, 176.8, 195.4 ppm. MS (EI): m/z= 383.44 (M^+). Anal. Calcd. For $C_{22}H_{25}NO_5$: C 68.91, H 6.57, N 3.65; Found: C 69.07, H 6.48, N 3.54 %.

Ethyl 4-(2,3-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate ***(6m)****:*

White solid (recrystallized from ethanol). m.p. = 220-221ºC. FT-IR (KBr): $\bar{\nu}$ = 3336 (NH), 1679 (C=O), 1665, 1512, 1328, 1251, 1218 (C-O) cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 0.99 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.28 (t, 3H, $OCH_2C\underline{H}_3$), 2.12 (s, 3H, CH_3), 2.18-2.23 (m, 4H, 2×CH_2), 3.72 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 4.03 (q, 2H, $OC\underline{H}_2CH_3$), 5.21 (s, 1H, CH), 6.49 (s, 1H, NH), 6.88-7.18 (m, 3H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1, 20.8, 25.3, 31.9, 34.2, 41.9, 44.8, 47.6, 52.7, 55.4, 59.1, 103.7, 123.2, 127.6, 129.8, 133.2, 140.8, 144.4, 145.1, 148.4, 163.2, 197.1 ppm. MS (EI): m/z = 383.44 (M^+). Anal. Calcd. For $C_{23}H_{29}NO_5$: C 69.15, H 7.32, N 3.51; Found: C 69.26, H 7.21, N 3.44 %.

3. Results and Discussion

The Co_3O_4 nanoparticles were first prepared by a facile method and the structure was confirmed by EDX, FT-IR, FE-SEM, VSM, XRD and TEM analysis, which were in good agreement with the literature [28].

The XRD pattern of the Co_3O_4nanoparticles (JCPDS File No. 74-1656) is shown in Fig. 1. The XRD line broadening determined the size of the magnetic nanoparticles using the Debye–Scherrer formula (D = Kλ/βcosθ), in which K is a constant (about 0.9), λ is the x-ray wavelength used in XRD (1.5418 Å) and θ is the position of the maximum diffraction peak β (full-width at half-maximum).

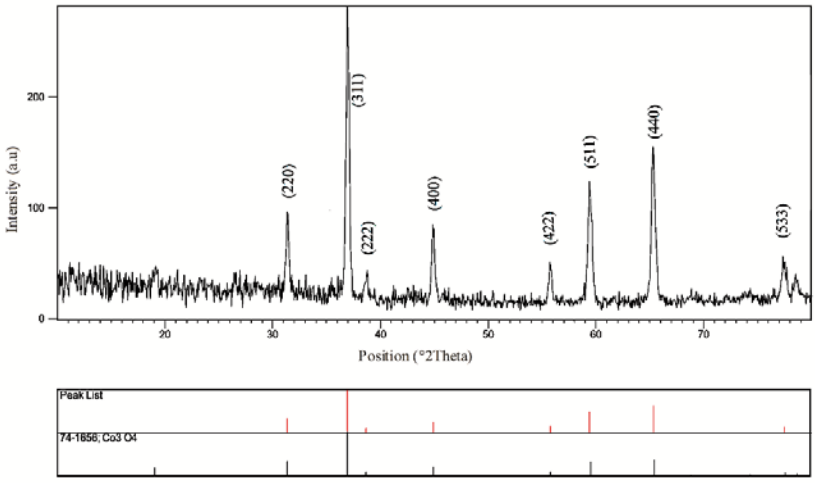


Fig. 1. XRD spectrum of Co_3O_4 NPs.

The major reflection indicated that the average size of Co_3O_4 nanoparticles was 18.8 nm. No peak for impurities was observed in the XRD patterns of sheets of Co_3O_4.

The Fourier transform infrared (FT-IR) spectrum of Co_3O_4 nanoparticles is shown in Fig. 2. The spinel structure of the Co_3O_4 nanoparticles was illustrated by two strong absorbance bands at 565 and 661 cm^{-1}. Stretching vibrations of the Co-O bands were observed at 565 and 661 cm^{-1}, which are in accordance with the reported IR spectra for Co_3O_4 nanoparticles [28].

The chemical purity of the sample was checked by energy dispersive x-ray spectroscopy (EDX) (Fig. 3). The EDX spectrum shows the presence of cobalt and oxygen as the only elements of the nanocatalyst.

The particle shape, size distribution and surface morphology of this particle were investigated by scanning electron microscopy (FE-SEM; Fig. 4). The SEM image show that the average size of Co_3O_4 is about 20 nm, which is completely agreement with the XRD pattern.

The magnetic properties of the Co_3O_4 nanoparticles were measured by vibrating sample magnetometer (VSM) at room temperature (Fig. 5).

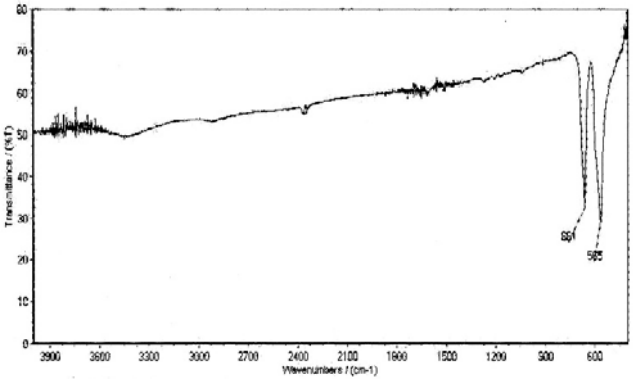


Fig. 2. FT-IR spectrum of Co_3O_4 NPs.

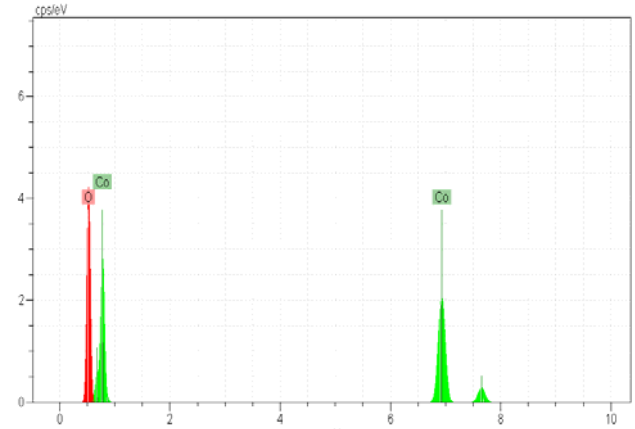


Fig. 3. EDX spectrum of Co_3O_4 NPs.

As seen, there is no hysteresis, coercivity or remanence in the synthesized nanoparticles, which confirms its super paramagnetic properties. The M versus H curves, show magnetization at saturation (Ms) was only 47.1 emu/g.

The size and morphology of Co_3O_4 nano particles were analyzed by transmission electron microscopy (TEM; Fig. 6). The results show that these nanocatalysts consist of spherical particles with a crystallite size of 15-20 nm. This is in good agreement with the results of the SEM image.

The results suggest that Co_3O_4 NPs can be used as an efficient catalyst for the synthesis of tetrahydrobenzo[*b*]pyran and polyhydroquinoline derivatives. To confirm this, the applicability of this catalyst was tested.

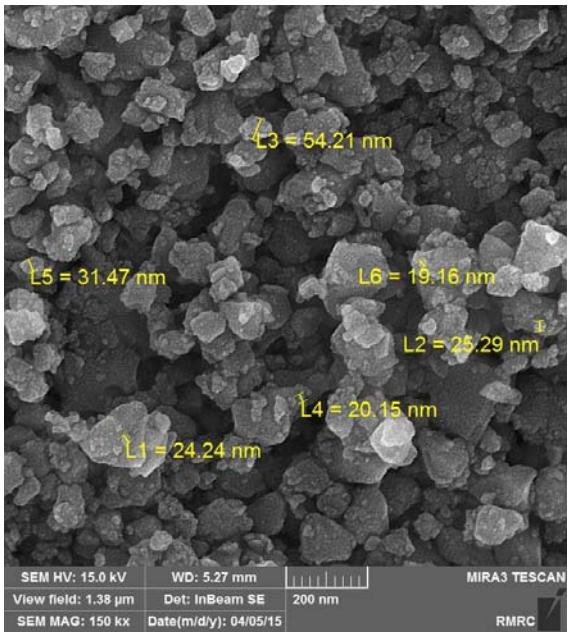


Fig. 4. SEM image of Co_3O_4 NPs.

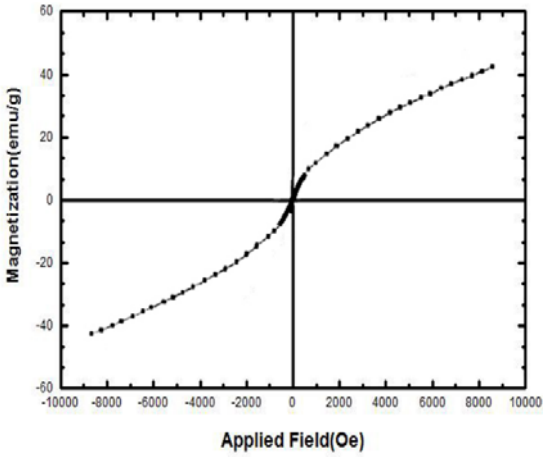


Fig. 5. VSM magnetization curve of the Co_3O_4 NPs.

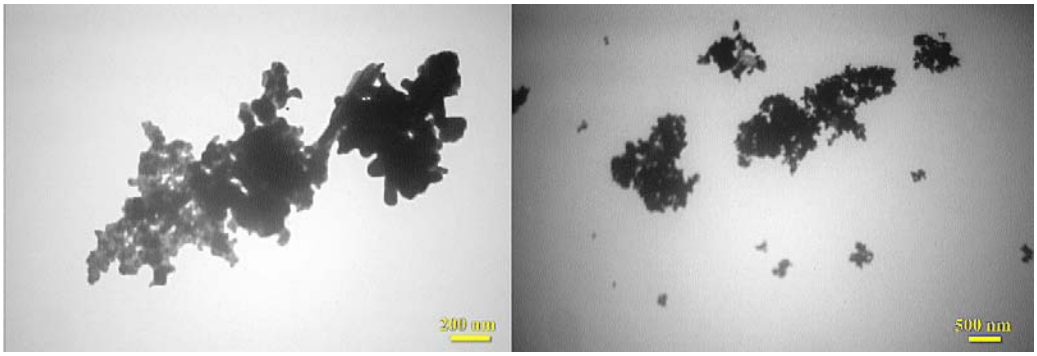


Fig. 6. TEM images of Co_3O_4 NPs.

In order to achieve the greenest and more efficient experimental conditions, the reaction of 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol) and malononitrile (1 mmol) was chosen as a model reaction for the synthesis of 2-amino-4-(4-chlorophenyl)-7,7- dimethyl-5- oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4f) (Scheme 1).

The influence of the catalyst was investigated in the synthesis of 4H-pyrans. No product was obtained when the reactions were carried out without catalyst (Table1; entry 1). Table 1 shows that, among the catalysts used, the Co_3O_4 nanoparticles reacted best. It was found that higher amounts of catalyst from the optimum point (0.02 g: 10% molar ratio) had no significant effect on yield and reaction time. In the next step, toluene, ethanol, acetonitrile solvents and also solvent-free conditions were examined in the model study. An excellent yield (98%) was obtained under solvent-free conditions at 100ºC (Table 1; entry 9).

To demonstrate the general applicability of the proposed method, the reaction of dimedone, aldehydes and malononitrile was carried out with different types of aromatic aldehydes containing electron-donating substituents and electron-withdrawing groups.

Table 1. Yields/reaction times for the preparation of 4f using various catalysts, solvent, temperature and amount of nanoparticles.[a]

Entry	Catalyst	Solvent	Temp. (ºC)	Time(min)	Yield (%)[b]
1	none	-	100	120	Trace
2	CuO	-	100	40	80
3	ZnO	-	100	22	88
4	CuI	-	100	25	82
5	MgO	-	100	15	80
6	AgI	-	100	30	85
7	NaOH	-	100	120	30
8	Co_3O_4(0.01gr)	-	100	15	70
9	Co_3O_4(0.02gr)	-	100	15	98
10	Co_3O_4(0.03gr)	-	100	15	98
11	Co_3O_4(0.02gr)	ethanol	reflux	80	35
12	Co_3O_4(0.02gr)	toluene	reflux	160	30
13	Co_3O_4(0.02gr)	acetonitrile	reflux	100	45
14	Co_3O_4(0.02gr)	-	60	15	50
15	Co_3O_4(0.02gr)	-	120	15	95

[a]Reaction conditions: 4-chlorobenzaldehyde, dimedone and malononitrile (1:1:1 molar ratio).
[b]Isolated yields.

The results showed that the corresponding tetrahydrobenzopyrans obtained in excellent yields (85% to 98%) in suitable time frames (Table 2). Aldehydes with electron-withdrawing groups such as NO_2 and Cl reacted more efficiently than electron-donating substituents such as OCH_3, CH_3. Moreover sterically hindered (ortho and meta) substitutes has a strong effect on the rate of synthesis of the pyrans. A comparison of the yields and reaction times between 3-nitro benzaldehyde and 4-nitro benzaldehyde demonstrated this effect clearly (Table 2; entries 8, 9). Polyhydroquinolines were then synthesized with different types of aromatic aldehydes. The model reaction included aldehydes (1mmol), 5,5-dimethyl-1,3-cyclohexaedione (1 mmol), ammonium acetate (1.2 mmol), ethyl acetoacetate (1 mmol) and Co_3O_4 nanoparticles as the catalyst at 100ºC under solvent-free conditions. As shown in Table 3, the four-component synthesis of aldehyde, dimedone, ammonium acetate and ethyl acetoacetate produced excellent yields (85% to 95%) in short reaction times with a comfortable work-up.

In recent years, practical applications for nanocatalysts in organic synthesis have increased to take advantage of benefits such as high catalytic activity, simple work-up, easy recovery, reusability and mild reaction conditions. Heterogeneous catalysts have performed better in comparison with other commercially-available catalyst. Table 4 compares Co_3O_4 nanoparticles with similar heterogeneous catalysts. The improvement in reaction rate, high catalytic activity, easier work-up, recoverability and excellent yield are some advantages of Co_3O_4 nanoparticles as a nanocatalyst.

The results suggest a plausible mechanism for the synthesis of tetrahydrobenzopyrans by catalysis of Co_3O_4 nanoparticles (Scheme 2). It was assumed that Co_3O_4 nanoparticles act as a Lewis acid by increasing the electrophilicity of the double and triple bonds and also carbonyl groups, through formation of a strong coordinate bond. Scheme 2 shows the Knoevenagel condensation reaction occurred by the reaction of aromatic aldehyde with malononitrile via an initial formation of α-cyanocinnamo-nitrile (I). Next the Michael addition of dimedone with intermediate (I) followed by intramolecular cyclization and rearrangement provided the final product.

Table 2. Synthesis of tetrahydrobenzopyran derivatives 4a-n using (0.02g) of Co_3O_4nanoparticles as catalyst under solvent-free conditions (Scheme 1).[a]

Entry	Aldehyde (R)	Product	Yield (%)[b]	Time (min)	m.p. (ºC)	
					Found	Reported[c]
1	C_6H_5	4a	91	22	226-228	227-229
2	4-$SCH_3C_6H_4$	4b	90	25	217-218	----------[d]
3	4-$CH_3C_6H_4$	4c	88	27	212-214	215-217
4	4-$OMeC_6H_4$	4d	87	30	200-202	195-197
5	4-FC_6H_4	4e	85	30	193-194	188-190
6	4-ClC_6H_4	4f	98	15	209-211	210-212
7	4-BrC_6H_4	4g	94	20	206-208	205-207
8	4-$NO_2C_6H_4$	4h	95	12	178-180	180-182
9	3-$NO_2C_6H_4$	4i	90	22	210-211	211-213
10	2,3-$(OMe)_2C_6H_4$	4j	85	35	168-170	----------[d]
11	4-$HCOC_6H_4$	4k	90	17	269-270	269-271
12	2,4-$(Cl)_2C_6H_4$	4l	90	22	119-121	120-122
13	4-$N(Me)_2C_6H_4$	4m	85	28	208-208	206-208
14	4-OHC_6H_4	4n	90	30	218-220	219-221

[a]Reaction conditions: dimedone (1 mmol), various aldehydes (1mmol)and malononitrile (1mmol)under solvent-free conditions at 100°C for various timesin the presence of 0.02g Co_3O_4 nanoparticles (Scheme 1).
[b]Isolated yield.
[c]From Ref. [35].
[d]New Product.

Table 3. Synthesis of polyhydroquinoline derivatives 6a-6n in presence of (0.02 g) Co_3O_4 NPs as catalyst under solvent-free conditions at 100ºC (Scheme 1).

Entry	Aldehyde (R)	Product	Yield (%)	Time (min)	m.p. (ºC)		Ref.
					Found	Reported	
1	C_6H_5	6a	88	50	203-204	202-204	[36]
2	4-$OMeC_6H_4$	6b	90	55	255-257	257-259	[36]
3	4-ClC_6H_4	6c	95	40	245-246	245-246	[36]
4	4-BrC_6H_4	6d	95	45	252-254	253-255	[36]
5	4-$NO_2C_6H_4$	6e	93	40	243-244	242-244	[36]
6	4-$CH_3C_6H_4$	6f	90	55	260-262	260-261	[36]
7	3-$NO_2C_6H_4$	6g	90	70	177-179	177-178	[36]
8	4-FC_6H_4	6h	92	50	185-186	184-186	[36]
9	2-$COOHC_6H_4$	6i	87	60	231-232	----------[c]	-
10	4-OHC_6H_4	6j	85	65	231-233	232-234	[36]
11	3-OHC_6H_4	6k	88	65	218-220	220-222	[36]
12	4-$N(Me)_2C_6H_4$	6l	85	60	262-264	263-264	[36]
13	2,3-$(OMe)_2C_6H_4$	6m	95	70	220-221	----------[c]	-
14	4-$HCOC_6H_4$	6n	92	50	297-298	294-296	[37]

[a]Reaction conditions: dimedone (1 mmol), various aldehydes (1 mmol)ammonium acetate(1.2 mmol) and ethyl acetoacetate (1 mmol) under solvent-free conditions the presence of Co_3O_4 (0.02g) at 100°C (Scheme 1).
[b]Isolated yield.
[c]New Products.

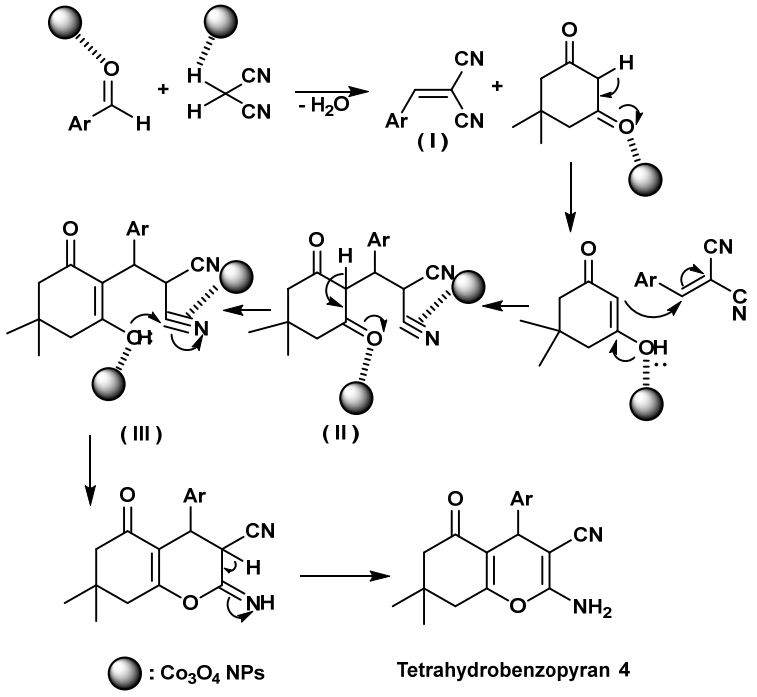
Reusability of the catalyst is significant for large-scale operations in industry. The recoverability of the catalyst was checked in the model study for the synthesis of pyrans. After the separation of the product, Co_3O_4 NPs were washed with H_2O and CH_2Cl_2 several times, dried; and reused for the same reactions. This process was performed over five runs without noticeable loss of activity. Fig. 7 shows that all of the reactions were carried out at the desired yields.

4. Conclusion

In this research, Co_3O_4 nanoparticles were used as recoverable catalyst for synthesis of polyhydroquinolines and tetrahydrobenzopyrans under solvent-free conditions. The advantages of this method are the reasonably simple work-up, little catalyst loading, short reaction time, non-hygroscopic quality and reusability of the Co_3O_4 nanoparticles which is in good agreement with green chemistry disciplines.

Table 4. The comparison between Co_3O_4 NPs with various catalyst in the synthesis of 4H-pyrans and polyhydroquinolines.

Entry	Catalyst	Time (min)	Yield (%)	Product	Ref.
1	FeF_3	60	92	polyhydroquinoline	[39]
2	ZnO NPs	20	86	polyhydroquinoline	[40]
3	$SnCl_2$/nano SiO_2	45	82	polyfunctionalized 4H-pyrans	[41]
4	CuO–CeO_2 nanocomposite	40	88	4H-benzo[b]pyrans	[42]
5	SBPPSP	35	89	2-amino-4H-pyran derivatives	[43]
6	Co_3O_4 NPs	15	98	4H-pyrans	This work
7	Co_3O_4 NPs	40	95	Polyhydroquinolines	This work



Scheme 2. Plausible mechanism for the synthesis of tetrahydrobenzopyrans.

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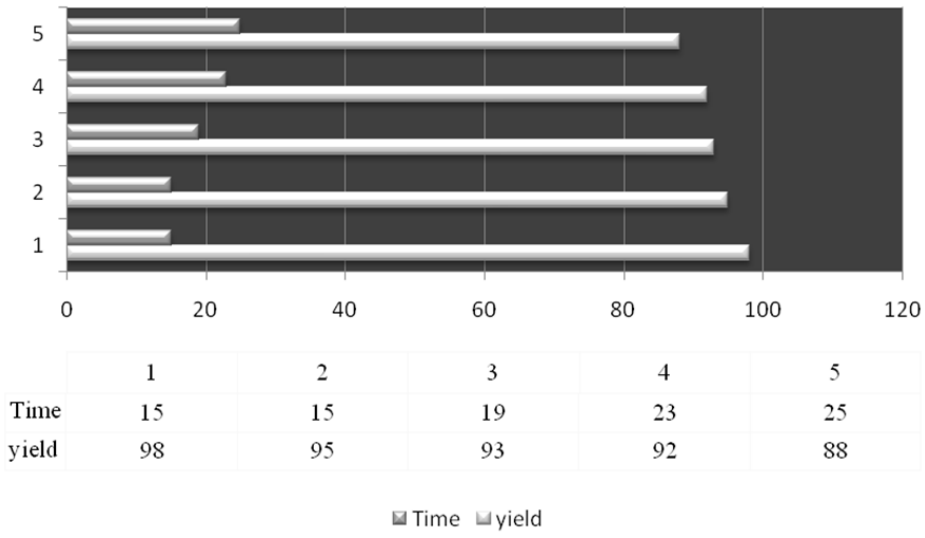

	1	2	3	4	5
Time	15	15	19	23	25
yield	98	95	93	92	88

Fig. 7. Reusability of the Co_3O_4 NPs in the synthesis of pyran (4f).

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