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Cobalt Nanoparticles-Mediated Catalyzed Synthesis of Pyrano [2,3-d]Pyrimidinones and Pyrano[2,3-c]Pyrazoles under Solvent-Free Conditions

J. Albadi[a*], M. Jalali[b] and H. A. Samimi[a]

[a] *Department of Chemistry, Faculty of Science, Shahrekord University, Shahrekord, Iran.*
[b] *National Petrochemical Company, Petrochemical Research and Technology Company, Tehran, Iran.*

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Abstract: In this research, cobalt based-nanoparticles (Co/Al_2O_3 nanocatalyst) are reported as an efficient recyclable catalyst for the synthesis of pyrano[2,3-d]pyrimidinones and pyrano[2,3-c]pyrazoles under solvent-free conditions. The nanocatalyst was prepared by the co-precipitation method and characterized by surface area measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) analyses. It can be easily recovered by simple filtration and recycled up to 5 consecutive runs with reliable activity. The present method provides other advantages, such as simple process, ease of work up, clean procedure and short reaction times.

Keywords: Pyrano[2,3-d]pyrimidinone, Pyrano[2,3-c]pyrazoles, Co/Al_2O_3 nanocatalyst, Solvent-free condition, Aldehyde.

Introduction

Nowadays, nanocatalysts have been revolutionized and received considerable attention to chemists in the laboratory and industry[1]. Metallic nanoparticles have already left their promise in different fields of scientific and technological research. Especially, supported-metallic nanoparticles play a significant role in nanoscience and nano-technology. It has been shown that supported-metallic nanoparticles exhibit higher stability and increased activity[2]. In this regard, nano-cobalt particles supported on alumina are important material systems in the field of heterogeneous catalysts. It has been reported that metal-support interactions may significantly affect the surface properties and catalytic activities[3]. Cobalt nanoparticles supported on alumina display an attractive performance in oxidation reactions because of the good mechanical properties of the alumina support[4-6]. Alumina-supported cobalt catalysts have been studied in various processes with respect to their activity in CO hydrogenation[7-8]. Nevertheless, to the best of our knowledge, there is no report about the use of alumina-supported cobalt nanoparticles as Lewis acid in multi-component organic synthesis reactions.

As part of our research program to develop efficient nanocatalysts[9-11], recently, we have reported on the preparation of a novel alumina-supported cobalt nanocatalyst (Co/Al_2O_3 nano-catalyst) and its catalytic activity in some organic reactions[12-13]. This nanocatalyst is safe, stable, easy to handle and its preparation is simple. Moreover, Co/Al_2O_3 nanocatalyst showed high activity and recyclability. Because of these properties, we decided to study the catalytic application of Co/Al_2O_3 nanocatalyst as a Lewis acid in the synthesis of some bio-logically important heterocyclic compounds.

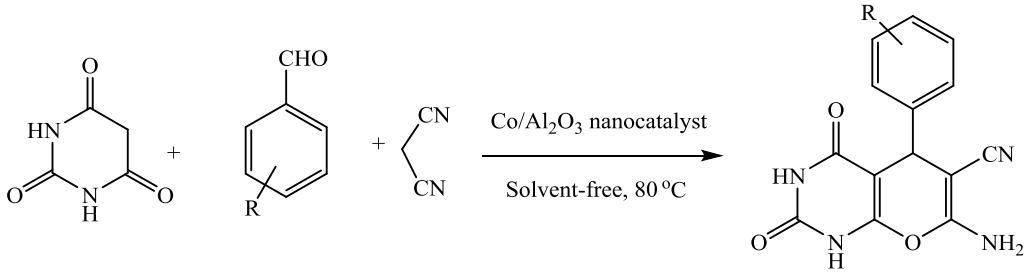
The synthesis of pyrano[2,3-d]pyrimidinones and pyrano[2,3-c]pyrazoles has received considerable attention because of their wide range of applications. These compounds are

[*]**Corresponding Author:** Jalal Albadi **Email**: chemalbadi@gmail.com

important heterocyclic compounds that have been broadly applied in various research fields, including synthetic, organic, medicinal, materials and biological chemistry[14-15]. Regarding the importance of pyrano[2,3-d]pyrimidinones, various synthetic procedures have been developed and the performance of various catalysts, especially heterogeneous ones, in the synthesis of these compounds was studied[16-24]. Moreover, a variety of heterogeneous catalysts were reported for the synthesis of pyrano[2,3-c]pyrazoles and various procedures have been developed[25-33]. It was observed that in the presence of these catalysts, good results were obtained. However, the development of new, efficient and clean approaches is still desirable and in demand.

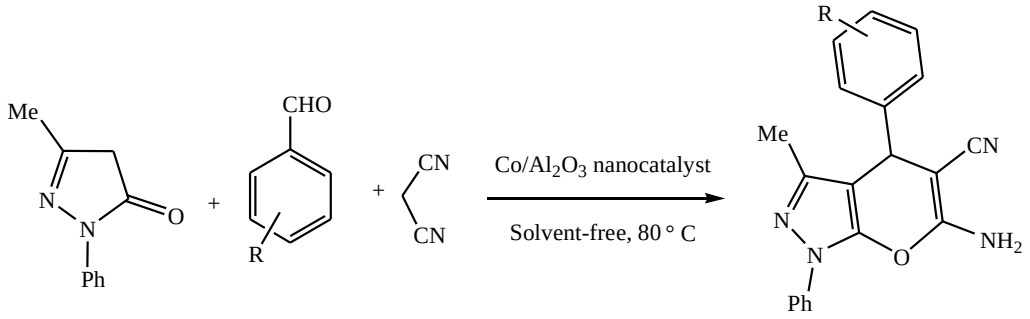
As mentioned, the performance of alumina-supported cobalt nanocatalyst (Co/Al_2O_3 nanocatalyst) as a Lewis acid has not been explored in the synthesis of heterocyclic compounds. Therefore, we report herein on the catalytic activity of Co/Al_2O_3 nanocatalyt in the multi-component synthesis of pyrano[2,3-d]pyrimidinones and pyrano[2,3-c]pyrazoles under solvent-free conditions (Schemes 1and 2).

Scheme 1. Synthesis of pyrano[2,3-d]pyrimidinones catalyzed by Co/Al_2O_3 nanocatalyst.



R=H, Cl, Br, F, CN, NO_2, Me, OMe, OH, $PhOCH_2$

Scheme 2. Synthesis of pyrano[2,3-c]pyrazoles catalyzed by Co/Al_2O_3 nanocatalyst.



R=H, Cl, Br, F, CN, NO_2, Me, OMe, OH

Materials and Methods

Chemicals were purchased from Merck. The products were characterized by comparison of their spectroscopic data (^{1}HNMR, ^{13}CNMR and IR) and physical properties with those reported in the literature. The BET specific surface area of the catalyst was measured by N_2 adsorption-desorption using an automated gas adsorption analyzer (Tristar 3020, Micrometrics). The samples were purged with N_2 gas for 3 h at 300^{o}C using VacPrep 061 degas system (Micrometrics). The XRD analysis was performed using an X-ray diffractometer (Panalytical X'Pert-Pro) with a Cu-Kα mono-chromatized radiation source and a Ni filter in the range 2θ = 5-100^o. The average crystallite size of the sample was determined based on Scherrer equation. A flame atomic absorption spectrophotometer (GBC 906AA) was used to determine the cobalt content of the catalyst. Scanning electron microscopy (SEM) was performed by a JEOL JSM-6500F instrument, equipped with an EDS analytical system, in order to study the morphology of the prepared catalyst as well as its composition. Transmission electron microscopy (TEM) analysis was performed using a JEOL JEM-2100 (200 kV) microscope with an EDS analytical system. Co/Al_2O_3 nanocatalyst was prepared by a co-precipitation method according to our previous reported article[13].

General Procedure for the Synthesis of Pyrano[2,3-d]Pyrimidinones and Pyrano[2,3-c]Pyrazoles

A mixture of aldehyde (1 mmol), malononitrile (1 mmol) and barbituric acid or 3-methyl-1-phenyl-2-pyrazolin-5-one (1 mmol), in the presence of Co/Al_2O_3 nanocatalyst (0.1 g), was heated in an oil bath (80 °C) for the appropriate times according to Tables 3 and 5. After reaction completion (monitored by TLC), the reaction mixture was cooled to room temperature, hot ethanol (8 mL) was added and the catalyst was recovered by filtration for subsequent use. The filtrate was evaporated and dried. Then, the solid residue was recrystallized in hot ethanol/water to afford pure products. The spectral data for the selected compounds was as follows.

7-amino-5-(4-nitrophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (Table 3, entry 2)

mp: 237-239 °C; IR (KBr) ν_{max}/cm^{-1}: 3053, 3000, 2925, 2830, 1720, 1610, 1505, 1380, 1282, 1210, 1165, 1140, 1060. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 4.21 (s, 1H), 7.12 (s, 2H), 7.29 (d, 2H), 7.44 (d, 2H), 11.05 (s, 1H), 12.06 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 36.63, 60.35, 89.98, 120.78, 130.89, 133.89, 141.94, 151.16, 153.88, 159.17, 161.72, 164.46.

7-amino-5-(4-chlorophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (Table 3, entry 3)

mp: 234-236 °C; IR (KBr) ν_{max}/cm^{-1}: 3055, 3015, 2920, 2830, 1725, 1610, 1515, 1380, 1280, 1210, 1160, 1145, 1060. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 4.22 (s, 1H), 7.14 (s, 2H), 7.19 (d, 2H), 7.35 (d, 2H), 11.06 (s, 1H), 12.05 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 36.60, 60.35, 89.97, 120.78, 130.89, 133.87, 141.90, 151.12, 153.88, 159.13, 161.70, 164.35.

7-amino-5-(4-bromophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (Table 3, entry 8)

mp: 234-236 °C; IR (KBr) ν_{max}/cm^{-1}: 3050, 3015, 2925, 2830, 1720, 1610, 1515, 1380, 1280, 1212, 1160, 1065. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 4.20 (s, 1H), 7.12 (s, 2H), 7.17 (d, 2H), 7.31 (d, 2H), 11.03 (s, 1H), 12.04 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 36.61, 60.32, 89.95, 120.70, 130.83, 133.85, 141.88, 151.11, 153.81, 159.13, 161.65, 164.34.

7-amino-2,4-dioxo-5-(p-tolyl)-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (Table 3, entry 9)

mp: 225-226 °C; IR (KBr) ν_{max}/cm^{-1}: 3055, 3015, 2920, 1715, 1615, 1515, 1380, 1280, 1215, 1165, 1065. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 1.60 (s, 3H), 4.22 (s, 1H), 6.76 (d, 2H), 6.87 (d, 2H), 7.12 (s, 2H), 11.02 (s, 1H), 12.03 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 32.33, 36.60, 60.31, 89.54, 114.20, 116.53, 118.80, 121.68, 131.10, 136.61, 159.14, 146.45, 163.36.

7-amino-5-(4-fluorophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (Table 3, entry 12)

mp: 269-271 °C; IR (KBr) ν_{max}/cm^{-1}: 3055, 3000, 2920, 1720, 1610, 1500, 1380, 1280, 1260, 1210, 1160, 1065. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 4.20 (s, 1H), 7.10 (s, 2H), 7.22 (d, 2H), 7.38 (d, 2H), 11.04 (s, 1H), 12.04 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 36.60, 60.35, 89.96, 120.75, 130.89, 133.89, 141.91, 151.15, 153.88, 159.19, 161.73, 164.45.

7-amino-5-(4-(benzyloxy)phenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (Table 3, entry 13)

mp: 152-153 °C; IR (KBr) ν_{max}/cm^{-1}: 3425, 3069, 2220, 1755, 1705, 1660, 1581, 1509, 1312, 1270, 1175. ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 5.02 (s, 1H), 5.23 (s, 2H), 6.90 (s, 1H), 7.10 (d, 2H), 7.23 (d, 2H), 7.94 (d, 2H), 8.20 (d, 1H), 8.33 (t, 2H), 11.15 (s, 1H), 12.27 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz), δ (ppm): 37.21, 60.78, 71.50, 90.36, 117.48, 120.90, 129.55, 129.78, 130.12, 134.96, 137.60, 139.05, 151.81, 156.56, 159.15, 161.64, 163.60.

6-amino-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (Table 5, entry 1)

mp:169-170 °C; IR (KBr) ν_{max}/cm^{-1}: 3390, 3310, 3200, 2905, 2195, 1650, 1425, 1300, 1015. ^{1}H NMR ($CDCl_3$, 400 MHz), *δ*: 1.77 (s, 3H), 4.77 (s, 2H), 5.29 (s, 1H), 7.21-7.26 (m, 3H), 7.31 (t, 2H), 7.30 (s, 2H), 7.33 (m, 1H), 7.46 (m, 2H), 7.76 (d, 2H), ^{13}C NMR (100 MHz, $CDCl_3$), *δ*: 12.76, 32.38, 60.75, 96.66, 117.36, 120.34, 125.89, 127.12, 128.36, 129.26, 130.41, 132.73, 136.33, 136.82, 142.91, 145.26, 158.67.

6-amino-3-methyl-4-(4-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (Table 5, entry 2)

mp: 193-195 °C; IR (KBr) ν_{max}/cm^{-1}: 3330, 3085, 2210, 1670, 1595, 1455, 1345, 1120, 107. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 1.77 (s, 3H), 4.72 (s, 1H), 7.46-7.58 (m, 3H), 7.62-7.71 (m, 4H), 7.82 (d, 2H), 7.88 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 13.51, 37.52, 58.14, 98.51, 110.81, 119.66, 119.95, 120.90, 126.94, 129.83, 130.15, 133.78, 138.55, 144.97, 145.93, 150.08, 160.49.

6-amino-4-(2,4-dichlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (Table 5, entry 3)

mp: 184-185 °C; IR (KBr) ν_{max}/cm^{-1}: 3395, 3315, 3205, 2900, 2205, 1640, 1405, 1305. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.92 (s, 3H), 4.81 (s, 2H), 5.30 (s, 1H), 7.17 (d, 1H), 7.27 (s, 1H), 7.37 (t, 1H), 7.46-7.51 (m, 3H), 7.68 (d, 2H). 13C NMR (100 MHz, $CDCl_3$), δ: 12.75, 33.49, 61.92, 97.57, 118.65, 121.28, 126.96, 128.06, 129.37, 129.68, 131.51, 133.94, 137.41, 137.87, 143.93, 146.05, 158.87.

6-amino-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (Table 5, entry 4)

mp: 176-177 °C; IR (KBr) ν_{max}/cm^{-1}: 3295, 3080, 2205, 1670, 1585, 1515, 1392, 1230, 1035. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 1.74 (s, 3H), 4.80 (s, 1H), 7.25-7.30 (m, 3H), 7.44-7.51 (m, 4H), 7.74 (d, 2H), 7.80 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 13.35, 37.52, 57.85, 97.93, 110.82, 118.87, 120.62, 120.92, 127.13, 129.76, 130.12, 133.50, 137.96, 144.85, 146.12, 150.09, 160.27.

6-amino-4-(3-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (Table 5, entry 5)

mp: 156-158 °C; IR (KBr) ν_{max}/cm^{-1}: 3300, 3295, 3190, 2195, 1660, 1642, 1205, 1050. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.85 (s, 3H), 4.82 (s, 2H), 5.31 (s, 1H), 7.19-7.24 (m, 5H), 7.32-7.68 (m, 5H), 7.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 13.23, 35.50, 57.93, 97.32, 110.41, 117.67, 120.61, 120.73, 126.33, 128.32, 129.65, 131.77, 136.15, 144.11, 145.85, 148.23, 159.41.

6-amino-4-(4-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (Table 5, entry 6)

mp: 172-174 °C; IR (KBr) ν_{max}/cm^{-1}: 3385, 3310, 2990, 2210, 1675, 1445, 1225, 1105, 1015. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.76 (s, 3H), 3.76 (3H), 4.54 (s, 1H), 6.88 (s, 2H), 7.13 (t, 1H), 7.18 (d), 7.23 (d, 2H), 7.26 (t, 2H), 7.52 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 13.41, 36.64, 45.23, 56.80, 96.52, 109.64, 115.16, 118.79, 120.12, 124.74, 127.81, 129.66, 132.83, 136.55, 143.83, 145.12, 150.12, 160.22.

Results and Discussion

To optimize the reaction conditions for the Co/Al_2O_3 catalyzed synthesis of pyrano[2,3-d]pyrimidinones, the reaction of 4-chlorobenzaldehyde with malononitrile and barbituric acid was chosen as a model reaction and its behavior was studied under a variety of conditions. The influences of various factors, such as type of solvent, catalyst amount and temperature were investigated. Different amounts of the Co/Al_2O_3 nanocatalyst (0.02, 0.05, 0.07, 0.1 and 0.12 g) were tested in various solvents, such as H_2O, EtOH, CH_2Cl_2, MeOH, CH_3CN as well as under solvent-free conditions, at various temperatures. As Table 1 exhibits, in the presence of 0.1 g of Co/Al_2O_3, the reaction was completed in 15 min to afford the corresponding product in an excellent yield of 94%. With an increase of the catalyst amount, the yield and time did not change. A catalyst mass of 0.10 g was hence chosen in this work as the optimum catalyst amount. Moreover, in the absence of Co/Al_2O_3 nanocatalyst, no product was obtained, confirming the important role of the Co/Al_2O_3 nanocatalyst in the synthesis of pyrano[2,3-d]pyrimidinone derivatives.

It was also established that when a solvent is used (water, ethanol, methanol, CH_3CN and CH_2Cl_2), the yield was low even though the reaction time was long. Moreover, the reaction rate was slow at room temperature and becomes enhanced at higher temperatures. Best results were obtained at 80 °C; higher temperatures did not cause any enhancement in the yield (Table 2). Summarizing, best yields were achieved by the reaction of 4-chlorobenzaldehyde, malononitrile and barbituric acid (1: 1: 1 mol ratio) in the presence of 0.1 g Co/Al_2O_3 under solvent-free conditions (Table 2).

Table 1: Effect of catalyst amount on the synthesis of pyrano[2,3-d]pyrimidinone[a].

Entry	Catalyst amounts (g)	Time (min)	Yield (%)[b]
1	-	180	-
2	0.02	120	Trace
3	0.05	100	45
4	0.07	45	72
5	0.1	20	94
6	0.12	20	94

[a] Reaction conditions: 4-chloro benzaldehyde (1 mmol), malononitrile (1 mmol), barbituric acid (1 mmol), under solvent-free condition. [b] Isolated pure products.

Table 2: Optimization of the reaction conditions.

Entry	Conditions [a]	Time (min)	Yield (%) [b]
1	H_2O/r.t.	180	-
2	H_2O/reflux	180	Trace
3	EtOH/r.t	180	-
4	EtOH/reflux	180	40
5	MeOH/r.t.	180	-
6	MeOH/reflux	180	Trace
7	CH_3CN/r.t.	180	-
8	CH_3CN/reflux	180	25
9	CH_2Cl_2/r.t.	180	-
10	CH_2Cl_2/reflux	180	Trace
11	Solvent-free/r.t.	180	Trace
12	Solvent-free/60 $^{\circ}$C	45	70
13	Solvent-free/80 $^{\circ}$C	15	94

[a] Reaction conditions: 4-chloro benzaldehyde (1 mmol), malononitrile (1 mmol), barbituric acid (1 mmol), in the presence of Co/Al_2O_3 nanocatalyst (0.1 g). [b] Isolated pure products.

The activity of various aromatic aldehydes under optimized conditions was then studied and the results are summarized in Table 3. It is clear that substitution with electron withdrawing or electron donating groups on the phenyl rings did not significantly influence the result of the reactions.

Table 3: Synthesis of pyrano[2,3-d]pyrimidinones catalyzed by Co/Al_2O_3 nanocatalyst.[a]

Entry	Aldehyde	Time (min)	Yield (%)	M.P. $^{\circ}$C [b]
1	C_6H_5CHO	20	94	206-207
2	4-$O_2NC_6H_4CHO$	12	95	237-239
3	4-ClC_6H_4CHO	15	94	234-236
4	3-ClC_6H_4CHO	18	93	240-241
5	2,4-ClC_6H_3CHO	12	94	240-242
6	4-CNC_6H_4CHO	15	91	251-253
7	3-OHC_6H_4CHO	22	91	161-163
8	4-BrC_6H_4CHO	12	94	234-236
9	4-MeC_6H_4CHO	15	92	225-226
10	4-$MeOC_6H_4CHO$	25	92	279-281
11	3-$MeOC_6H_4CHO$	15	90	200-202
12	4-FC_6H_4CHO	15	93	269-271
13	4-$C_6H_5CH_2OC_6H_4CHO$	25	91	152-153

[a] Reaction conditions: Aldeyde (1 mmol), barbituric acid (1 mmol), malononitrile (1 mmol), Co/Al_2O_3 nanocatalyst (0.1 g), under solvent-free condition. [b] Products were characterized by comparison of their spectroscopic data (NMR and IR) and melting points with those reported in the literature[23].

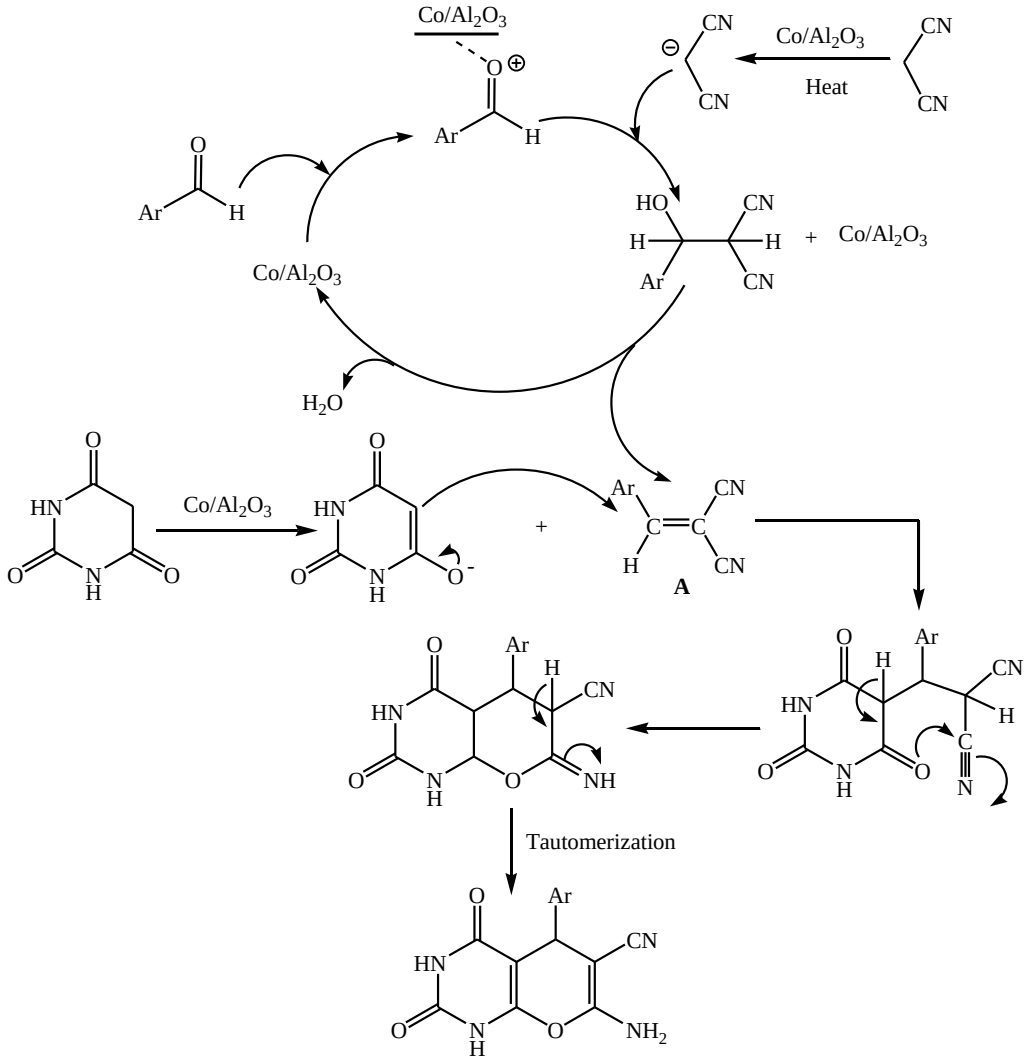
In all experiments, work-up procedure is so simple, and the products were cleanly isolated by simple filtration and recrystallized from hot ethanol. In these processes, no by-product was found in the reaction mixture; the corresponding products were obtained in high yields. Moreover, in all reactions, the Co/Al_2O_3 nanocatalyst could be separated and reused. The reusability of the Co/Al_2O_3 nanocatalyst was tested in the model reaction od 4-chlorobenzaldehyde. After reaction completion, the catalyst was separated, dried and stored for another consecutive run. This process was repeated for 5 runs and no significant decrease in the catalytic activity was observed (Table 4). A plausible mechanism for the three-component synthesis of pyrano[2,3-d]pyrimidinones catalyzed by Co/Al_2O_3 nano-catalyst is shown in scheme 3.

Table 4: Recyclability of Co/Al_2O_3 nanocatalyst.

Run	1	2	3	4	5
Time (min)	15	15	15	25	35
Yield (%) [a]	94	94	92	90	90

[a] Ioslated pure products.

Scheme 3. The proposed mechanism for the three-component synthesis of pyrano[2,3-d]pyrimidinones catalyzed by Co/Al_2O_3 nanocatalyst.



In the same way, synthesis of pyrano[2,3-c]pyrazoles in the presence of Co/Al_2O_3 nanocatalyst was also studied *via* three-component reaction of aromatic aldehydes, malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one. In a typical experimental procedure, the reaction of 4-chloro benz-aldehyde, malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one was investigated. It was found that the best results were achieved by running the reaction of 4-chloro benzaldehyde, malono-nitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one

(with 1: 1: 1 mol ratio) in the presence of 0.1 g Co/Al_2O_3 nanocatalyst at 80 °C in the absence of the solvent. Using these optimized conditions, the reaction of various aromatic aldehydes was explored. From Table 5, it is clear that aromatic aldehydes containing electron-donating or electron-withdrawing groups efficiently reacted under solvent-free conditions to afford the desired pyrano[2,3-c]pyrazoles in high yields (Table 5).

In these reactions, products were separated with simple filtration and evaporation of the solvent. Solid products were recrystallized from hot ethanol and obtained in high yields during the short reaction times. The experimental procedure with this catalyst was very simple and the catalyst can be recovered by simple filtration. Moreover, recyclability of the catalyst for the reaction of 4-chloro benzaldehyde, malononitrile and 3-methyl-1-phenyl-2-pyrazolin-5-one under optimized conditions was investigated. After reaction completion, Co/Al_2O_3 nanocatalyst was recovered by filtration. Then, it was washed with hot ethanol, dried and used for supplementary runs. The catalyst showed a sustained performance after 5 consecutive runs with no loss of activity (Table 6).

Table 5: Synthesis of pyrano[2,3-c]pyrazoles catalyzed by Co/Al_2O_3 nanocatalyst[a].

Entry	Aldehyde	Time (min)	Yield (%)	M.P. °C [b]
1	C_6H_5CHO	18	93	169-170
2	4-$O_2NC_6H_4CHO$	9	93	193-195
3	2,4-ClC_6H_3CHO	12	94	184-185
4	4-ClC_6H_4CHO	12	93	176-177
5	3-ClC_6H_4CHO	15	92	156-158
6	4-$MeOC_6H_4CHO$	22	91	172-174
7	4-MeC_6H_4CHO	20	90	177-178
8	4-FC_6H_4CHO	15	92	168-170
9	4-OHC_6H_4CHO	25	90	209-210
10	4-CNC_6H_4CHO	15	91	217-219

[a]Reaction conditions: Aldeyde (1 mmol), 3-methyl-1-phenyl-2-pyrazolin-5-one (1 mmol), malononitrile (1 mmol), Co/Al_2O_3 nanocatalyst (0.07 g), under solvent-free condition. [b] Products were characterized by comparison of their spectroscopic data (NMR and IR) and melting points with those reported in the literature[25-27].

Table 6: Recyclability study of Co/Al_2O_3 nanocatalyst.

Run	1	2	3	4	5	1
Time (min)	12	12	15	22	30	12
Yield (%) [a]	93	91	91	91	89	93

[a] Ioslated pure products.

Conclusions

In conclusion, in this work, the Co/Al_2O_3 nanocatalyst was proven to be an efficient recyclable catalyst for the multi-component synthesis of pyrano[2,3-d]pyrimidinones and pyrano[2,3-c]pyrazoles under solvent-free conditions. The catalyst confirmed a satisfactory activity after 5 consecutive runs. Cleanliness of the procedure, ease of work-up and short reaction times with high yields make this method an applicable procedure for the synthesis of pyrano[2,3-d]pyrimidinones and pyrano[2,3-c]pyrazoles.

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