



## Original Research article

## Alumina-Supported Cobalt Nanoparticles Efficiently Catalyzed the Synthesis of Chromene Derivatives under Solvent-Free Condition



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### KEYWORDS

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Nanocatalyst

Resorcinol

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Solvent-free condition

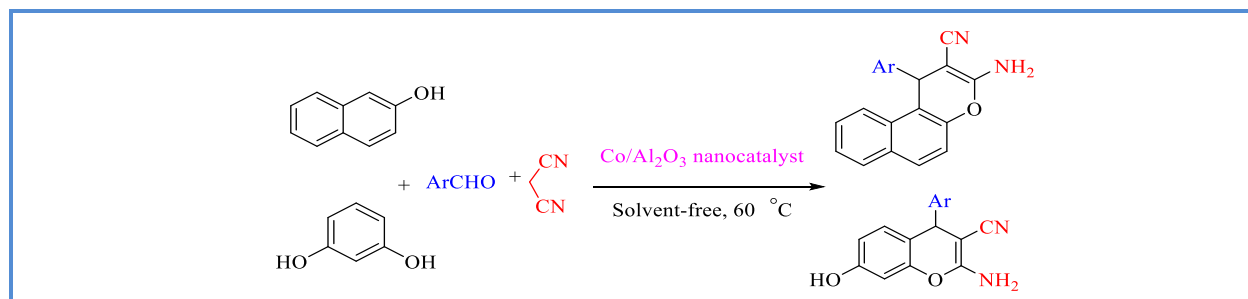
### ABSTRACT

In this research study, an efficient approach is reported for the solvent-free synthesis of various chromene derivatives catalyzed by alumina-supported cobalt nanoparticles in high yields. Alumina-supported cobalt nanoparticles (Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst), efficiently catalyzed the reaction between the resorcinol or 2-hydroxy naphthalene with benzaldehyde and malononitrile into chromene derivatives in high efficiency. This procedure allowed us to obtain corresponding products in short reaction times, simple work-up, and high yields. Experimental procedure with Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst is very simple and the catalyst is easily removed by filtration. The catalyst was also found to be recyclable and can catalyze synthesis of the chromenes up to 5 times well.

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### Graphical Abstract

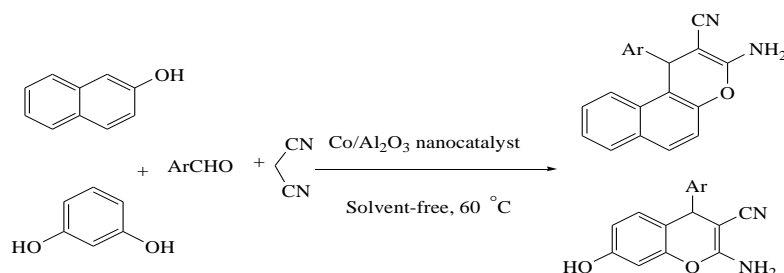


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## Introduction

Nanocatalysts have revealed interesting features that make them attractive catalysts for the catalyz of organic synthesis and industrial processes. Nanocatalysts have been extensively investigated for various organic synthesis and industrial reactions. The potential use of nanocatalysts in the fine chemical production are promising [1, 2]. Among them, supported-metallic nanocatalysts are the most promising and have been received increasing attention due to their high activity, selectivity, stability and recyclability. Supported-metallic nanocatalysts are composed of several components and can show the properties of diverse components in the identical structure [3].

Alumina is an attractive metal oxide as it is extensively used industrially as filler, adsorbent, drying agent, catalyst, catalyst support and reagent [4]. Alumina has large surface area and highly absorbent exteriors available to substrates. The act of various alumina-supported catalysts were investigated in some chemical process. It has been reported that, the metal-support interactions can considerably advance physical properties of the surface of the catalyst and thus it's catalytic activity [5-7]. Recently, we have reported the preparation of alumina-supported cobalt nanoparticles ( $\text{Co}/\text{Al}_2\text{O}_3$  nanocatalyst) and its function on the organic reactions [8, 9]. In extension of our studies on this nanocatalyst and others [10-12], herein, we report the catalytic application of  $\text{Co}/\text{Al}_2\text{O}_3$  nanocatalyst as an efficient recyclable catalyst on the multi-component synthesis of various chromenes from reaction of resorcinol or 2-hydroxy naphthalene with benzaldehyde and malononitrile under solvent-free conditions (Scheme 1).



**Scheme 1.**  $\text{Co}/\text{Al}_2\text{O}_3$  nanocatalystcatalyzed multi-component synthesis of aminochromenes

Chromenes signify an important group of compounds being the main component of many natural products, and are broadly employed as cosmetics, pigments and potential biodegradable agrochemicals [13]. Also, chromenes received considerable interest from many pharmaceuticals and organic chemists since of the broad variety of their biological and pharmaceutical properties such as antisterility and anticancer agents [14]. Therefore, the synthesis of chromenes is very important in

organic chemistry and various catalytic systems have been investigated for the synthesis of these compounds [15-29]. However, efforts to provide new, green and effective methods for the synthesis of these compounds continue to be sought.

## Experimental

All the materials were purchased from the Merck chemical company. All products were synthesized with high yields and identified by comparing with the physical properties and spectroscopy analysis of the authentic samples. Yields refer to isolated pure products.  $\text{Co}/\text{Al}_2\text{O}_3$  nanocatalyst was prepared according to our previous research [8].

## General procedure

A mixture of an aromatic aldehyde (1 mmol), malononitrile (1 mmol), and resorcinol or 2-hydroxy naphthalene (1 mmol), in the presence of  $\text{Co}/\text{Al}_2\text{O}_3$  nanocatalyst (0.1 g) in an oil bath was stirred under the solvent-free condition at 60 °C. After completion of the reaction, the hot acetone was added to the reaction mixture and catalyst was removed by simple filtration. The resulting solution was evaporated and obtained solid products were purified with hot ethanol to produce pure products.

## Results and discussion

The catalyst was prepared according to the method reported in our previous research. It was characterized using the X-ray diffraction (XRD) analysis, BET surface area analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS) [8].

**Table 1.** Optimization of reaction conditions<sup>a</sup>

Entry	Condition	Catalyst (g)	Time (min)	Yield (%) <sup>b</sup>
1	H <sub>2</sub> O/reflux	-	120	-
2	H <sub>2</sub> O/reflux	0.05	120	Trace
3	H <sub>2</sub> O/reflux	0.10	120	20
4	EtOH/reflux	-	120	-
5	EtOH/reflux	0.10	120	50
6	MeOH/reflux	0.10	120	25
7	MeCN/reflux	0.10	120	Trace
8	CH <sub>2</sub> Cl <sub>2</sub> /reflux	0.10	120	Trace
9	Solvent-free/ 60 °C	0.05	90	55
10	Solvent-free/ 80 °C	0.07	90	55
11	Solvent-free/ 60 °C	0.07	60	65
12	Solvent-free/ 80 °C	0.07	60	65
13	Solvent-free/ 60 °C	0.10	25	94
14	Solvent-free/ 80 °C	0.10	25	94

<sup>a</sup> Reaction conditions: Benzaldehyde (1 mmol), resorcinol (1 mmol), malononitrile (1 mmol), under solvent-free conditions. <sup>b</sup> Yield refers to isolated pure products

To optimize the reaction conditions, the reaction between the benzaldehyde, resorcinol and malononitrile was selected as a model reaction and their behaviour under different conditions were investigated. The effect of the main factors such as solvent, temperature and catalyst amounts were studied. In the absence of Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst, it was found that the reaction did not proceed and no product was obtained, which indicated the necessity of the catalyst for this reaction. The experiments showed that in the presence of 0.1 gr of the catalyst, the best results were obtained and the desired product was produced in the shortest possible time in the highest yield. When a smaller amount of the catalyst used, results were not satisfactory. An increase in the catalyst amount did not significantly effect on the yield and time of the reaction (Table 1). The model reaction was studied in various solvents such as water, ethanol, methanol, dichloromethane, acetonitrile, as well as solvent-free conditions, and the best result was obtained under solvent-free condition at 60 °C (Table 1). Finally, solvent-free conditions at 60 °C and in the presence of 0.1 gr of the catalyst were selected as the best conditions. After analyzing the reaction conditions, reaction of various aldehydes was investigated for the synthesis of chromene derivatives. Various aromatic aldehydes including electron-withdrawing groups such as nitro, nitrile and electron-donating groups such as methyl and methoxy were investigated (Table 2). The results showed the groups on aromatic ring had no noticeable effect on the reactions and desired products were synthesized in high yields and in short reaction times.

**Table 2.** Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst catalyzed multi-component synthesis of aminochromenes from resorcinol<sup>a</sup>

Entry	Aldehyde	Time (min)	Yield (%) <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub> CHO	25	94
2	4-ClC <sub>6</sub> H <sub>4</sub> CHO	20	94
3	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	20	93
4	2-ClC <sub>6</sub> H <sub>4</sub> CHO	25	90
5	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	25	91
6	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	20	90
7	4-BrC <sub>6</sub> H <sub>4</sub> CHO	18	93
8	4-MeOC <sub>6</sub> H <sub>4</sub> CHO	35	93
9	4-HOC <sub>6</sub> H <sub>4</sub> CHO	45	93

<sup>a</sup> Reaction conditions: Aldehyde (1 mmol), resorcinol (1 mmol), malononitrile (1 mmol), Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst (0.1 g), under solvent-free conditions. <sup>b</sup> Isolated pure products. Products were characterized by comparison of their spectroscopic data (NMR and IR) and melting points with those reported in the literature [19]

Moreover, the reaction of 2-hydroxy naphthalene performed efficiently compared to that of the reactions with resorcinol and in all cases, products were provided in high yields (Table 3). All the reactions were performed under the solvent-free conditions and completely heterogeneous reaction conditions. Corresponding products have been identified by comparison of the melting points and the analytical data (IR, NMR) of those reported for the authentic samples. The results

showed that the Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst as a simple and effective catalyst could well accelerate the synthesis of various derivatives of chromenes. No by-product was produced in these reactions, and the extracting and purifying products procedure is very simple. Reactions in the presence of Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst were clean and all the corresponding products were prepared after simple filtration and purification by recrystallization from hot ethanol. Moreover, experimental procedure with Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst is very convenient and the catalyst is easily removed by simple filtration.

**Table 3.** Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst catalyzed multi-component synthesis of aminochromenes from 2-hydroxy naphthalene<sup>a</sup>

Entry	Aldehyde	Time (min)	Yield (%) <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub> CHO	30	93
2	4-ClC <sub>6</sub> H <sub>4</sub> CHO	25	93
3	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	18	94
4	2-ClC <sub>6</sub> H <sub>4</sub> CHO	22	91
5	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	20	92
6	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	20	91
7	4-BrC <sub>6</sub> H <sub>4</sub> CHO	22	93
8	4-MeOC <sub>6</sub> H <sub>4</sub> CHO	35	93
9	4-HOC <sub>6</sub> H <sub>4</sub> CHO	45	89

<sup>a</sup> Reaction conditions: Aldehyde (1 mmol), 2-hydroxy naphthalene (1 mmol), malononitrile (1 mmol), Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst (0.1 g), under solvent-free conditions. <sup>b</sup> Isolated pure products. Products were characterized by comparison of their spectroscopic data (NMR and IR) and melting points with those reported in the literature [29]

Recyclability of a catalyst is an important feature. So this feature was studied. For this purpose, the reaction between resorcinol, benzaldehyde and malononitrile was investigated. It was observed that the Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst was able to catalyze the reaction up to 5 times without significantly changing in its catalytic activity. After reaction completion, Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst was washed with hot ethanol, dried and stored for another following reaction run (Table 4).

**Table 4.** Recyclability study of Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst upon the multi-component synthesis of aminochromenes from resorcinol<sup>a</sup>

Run	1	2	3	4	5
Time (min)	25	25	25	30	30
Yield (%) <sup>b</sup>	94	93	93	92	90

<sup>a</sup> Reaction conditions: Benzaldehyde (1 mmol), resorcinol (1 mmol), malononitrile (1 mmol), under solvent-free conditions. <sup>b</sup> Isolated yield

The catalyst recycling ability was also investigated on the chromenes synthesis reaction using 2-hydroxy naphthalene. Thus, the reaction of benzaldehyde, 2-hydroxy naphthalene and malononitrile was chosen as the model reaction. As revealed in the Table 5, the results show that the catalyst can be recovered well up to 5 times without any loss of its efficiency and the corresponding product was prepared in high yields after 1-5 runs, respectively (Table 5).

**Table 5.** Recyclability study of Co/Al<sub>2</sub>O<sub>3</sub> nanocatalyst upon the multi-component synthesis of aminochromenes from 2-hydroxy naphthalene<sup>a</sup>

Run	1	2	3	4	5
Time (min)	30	35	35	40	45
Yield (%) <sup>b</sup>	93	93	91	90	89

<sup>a</sup> Reaction conditions: Benzaldehyde (1 mmol), resorcinol (1 mmol), malononitrile (1 mmol), under solvent-free conditions. <sup>b</sup> Isolated yield

## Conclusions

In this research study, the catalytic application of the CO/Al<sub>2</sub>O<sub>3</sub> nanocatalyst as an effective and recyclable catalyst for the multi-component synthesis of various derivatives of chromene was assessed. CO/Al<sub>2</sub>O<sub>3</sub> nanocatalyst, as a heterogeneous catalyst, was able to accelerate the synthesis of the chromenes in short reaction times, and the corresponding products are produced in high yields. The proposed method was found to be a clean method and product separation was found to be easy. The catalyst was also recyclable and able to catalyze multi-component synthesis of chromenes up to 5 times well.

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