

Green Synthesis of 2-Amino-2-Chromene Derivatives Mediated by Cobalt Oxide Nanoparticles

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Abstract: Green chemistry has emerged as an important and rapidly growing approach for the development of sustainable and environmentally benign synthetic methodologies. The present study describes the green synthesis of cobalt oxide (Co_3O_4) nanoparticles and their application as efficient heterogeneous catalysts for the synthesis of biologically important 2-amino-2-chromene derivatives. The cobalt oxide nanoparticles were synthesized using an eco-friendly precipitation method and characterized using UV-Visible spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD) analysis. UV-Visible spectroscopic analysis confirmed nanoparticle formation through characteristic absorption bands, while SEM analysis revealed nanosized particles with nearly spherical morphology and moderate agglomeration. XRD studies confirmed the crystalline cubic spinel structure of Co_3O_4 nanoparticles.

The synthesized nanoparticles were successfully utilized as reusable heterogeneous catalysts in one-pot multicomponent reactions involving aromatic aldehydes, malononitrile, and resorcinol or α -naphthol for the synthesis of 2-amino-2-chromene derivatives. The developed catalytic method exhibited several advantages including excellent product yields, shorter reaction times, mild reaction conditions, easy work-up procedures, and reduced environmental impact. Spectroscopic characterization further confirmed the successful formation of chromene derivatives. The study demonstrates that cobalt oxide nanoparticles are highly efficient green catalysts for sustainable heterocyclic synthesis and environmentally friendly organic transformations.

Keywords: Green chemistry, cobalt oxide nanoparticles, chromene derivatives, multicomponent reactions, nanocatalysis, heterocyclic compounds.

I. INTRODUCTION

Green chemistry has emerged as an important approach in modern chemical research for the development of environmentally sustainable synthetic methodologies. It mainly focuses on the reduction of hazardous substances, prevention of waste generation, improvement of atom economy, and development of eco-friendly reaction processes. Conventional organic synthesis methods often involve the use of toxic solvents, harsh reaction conditions, corrosive reagents, and non-recyclable catalysts, which may cause environmental pollution and safety concerns. Therefore, green synthetic approaches have gained considerable importance in sustainable chemistry.

Nanotechnology has also become a rapidly developing field because nanoparticles exhibit unique physicochemical properties such as high surface area, enhanced catalytic activity, improved electronic behavior, and superior reaction efficiency compared to bulk materials. Transition metal oxide nanoparticles are widely utilized in various applications including catalysis, sensors, drug delivery systems, photocatalysis, and environmental remediation due to their excellent functional properties.



Among different metal oxide nanoparticles, cobalt oxide nanoparticles have attracted significant attention because of their excellent catalytic activity, thermal stability, semiconducting behavior, and high surface reactivity. These nanoparticles are widely used in photocatalysis, electrochemical devices, batteries, gas sensors, and green organic synthesis. Their high catalytic efficiency and recyclability make them promising materials for environmentally benign catalytic applications.

Chromene derivatives represent an important class of heterocyclic compounds with significant biological and pharmaceutical activities. In particular, 2-amino-2-chromene derivatives exhibit a wide range of biological properties including anticancer, antimicrobial, antioxidant, anti-inflammatory, antiviral, and antidiabetic activities. Due to these pharmacological properties, chromene derivatives are extensively used in medicinal chemistry, pharmaceutical intermediates, biologically active molecules, and heterocyclic synthesis.

II. OBJECTIVES OF THE STUDY

The primary objective of the present study was to synthesize cobalt oxide nanoparticles using an eco-friendly and sustainable method and to characterize the synthesized nanoparticles using various spectroscopic and analytical techniques. Another major objective was to utilize the prepared Co_3O_4 nanoparticles as efficient heterogeneous nanocatalysts for the synthesis of biologically important 2-amino-2-chromene derivatives.

The study also aimed to develop a sustainable multicomponent synthetic methodology with reduced environmental impact and improved reaction efficiency. In addition, an attempt was made to evaluate the catalytic efficiency of cobalt oxide nanoparticles in promoting multicomponent reactions under mild conditions. Spectral characterization of the synthesized chromene derivatives was also carried out to confirm their structural and chemical properties.

III. SYNTHESIS OF COBALT OXIDE NANOPARTICLES

Cobalt nitrate was initially dissolved in distilled water to obtain a homogeneous pink-colored precursor solution. Sodium hydroxide solution was then added dropwise under continuous stirring conditions, and the pH of the reaction mixture was maintained around 10–11. During this process, cobalt hydroxide precipitate was formed, indicating the initiation of nanoparticle synthesis.

The obtained precipitate was separated by filtration and repeatedly washed with distilled water and ethanol to remove impurities and unreacted substances. The purified product was dried at 80–100°C and subsequently calcined at 400–500°C to obtain crystalline cobalt oxide (Co_3O_4) nanoparticles. The formation of Co_3O_4 nanoparticles was confirmed by the appearance of characteristic black coloration after calcination.

IV. CHARACTERIZATION OF COBALT OXIDE NANOPARTICLES

UV–Visible Spectroscopy

UV–Visible spectroscopic analysis was carried out to study the optical properties and electronic transitions of the synthesized cobalt oxide nanoparticles. In semiconductor nanoparticles, electron excitation occurs from the valence band to the conduction band upon absorption of electromagnetic radiation. The synthesized Co_3O_4 nanoparticles exhibited strong absorption in the UV region between 250–350 nm along with extended absorption in the visible region between 400–600 nm. These absorption characteristics confirmed the semiconducting behavior of cobalt oxide nanoparticles and indicated the successful formation of nanosized particles.

FTIR Analysis

FTIR analysis was performed to identify the functional groups present in the synthesized nanoparticles and to confirm cobalt oxide formation. The broad absorption band observed in the range of 3400–3320 cm^{-1} was attributed to O–H



stretching vibrations, while peaks appearing between 1620–1580 cm^{-1} indicated metal–oxygen interactions. The characteristic absorption band observed in the range of 600–700 cm^{-1} corresponded to Co–O stretching vibrations, confirming the formation of cobalt oxide nanoparticles. The FTIR results indicated successful conversion of the precursor compounds into cobalt oxide nanostructures.

X-Ray Diffraction (XRD) Analysis

X-ray diffraction analysis was carried out to determine the crystalline structure and phase purity of the synthesized cobalt oxide nanoparticles. The analysis follows Bragg's law:

$$n\lambda = 2d \sin \theta$$

The diffraction peaks observed at 2θ values of 31.3°, 36.8°, 44.8°, 59.3°, and 65.2° corresponded to the crystal planes (220), (311), (400), (511), and (440), respectively. These characteristic peaks confirmed the formation of cubic spinel Co_3O_4 nanoparticles. The sharp diffraction peaks indicated good crystallinity, while peak broadening confirmed the nanoscale particle size of the synthesized nanoparticles.

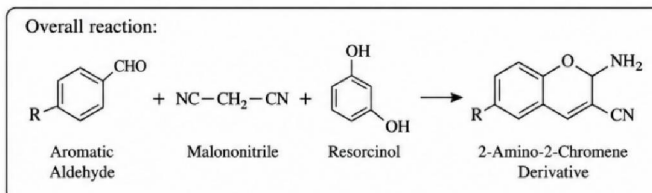
Scanning Electron Microscopy (SEM)

SEM analysis revealed that the synthesized cobalt oxide nanoparticles possessed spherical morphology with nanoscale dimensions, rough surface texture, and moderate agglomeration. The nanoparticles exhibited porous surface characteristics, which provide high surface area and enhance catalytic activity. The porous nanostructure also improves adsorption behavior and reaction efficiency, making the synthesized Co_3O_4 nanoparticles effective catalysts for green organic synthesis.

SYNTHESIS OF 2-AMINO-2-CHROMENE DERIVATIVES

Reaction Principle

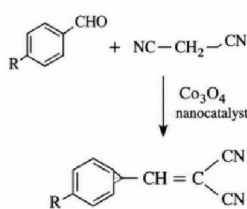
- One-pot multicomponent reaction involving:
 - aromatic aldehyde,
 - malononitrile,
 - and resorcinol/ α -naphthol.



Reaction Mechanism

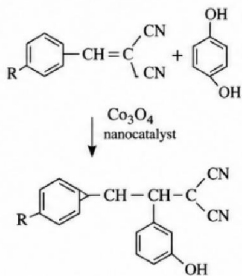
Step 1: Knoevenagel Condensation

- Aromatic aldehyde reacts with malononitrile.



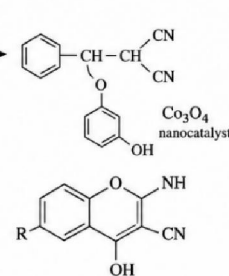
Step 2: Michael Addition

- Resorcinol attacks activated intermediate.



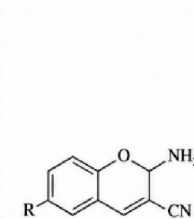
Step 3: Cyclization

- Intramolecular ring closure occurs.



Step 4: Tautomerization

- Formation of stable chromene derivative.



Where, R = H, CH₃, OCH₃, Cl, Br, NO₂, OH, etc.



V. EXPERIMENTAL PROCEDURE

The synthesis of 2-amino-2-chromene derivatives was carried out using a one-pot multicomponent reaction involving aromatic aldehyde (1 mmol), malononitrile (1 mmol), and resorcinol or α -naphthol (1 mmol) in the presence of a catalytic amount of Co_3O_4 nanoparticles. Ethanol was used as a green solvent due to its environmentally friendly nature and good solubility characteristics.

The reaction mixture was heated under reflux conditions at 60–80°C with continuous stirring. The progress of the reaction was monitored periodically using thin layer chromatography (TLC). The reaction was generally completed within 30–90 minutes depending on the nature of the substituted aromatic aldehyde used. After completion of the reaction, the product was isolated by filtration, purified through recrystallization, and dried to obtain pure 2-amino-2-chromene derivatives.

VI. OBSERVATION TABLE

Aldehyde Used	Product	Yield (%)	Melting Point (°C)
Benzaldehyde	2-Amino-4-phenyl chromene	85–92	210–214
4-Methylbenzaldehyde	p-Methyl chromene	80–90	218–222
4-Methoxybenzaldehyde	p-Methoxy chromene	78–88	225–230
4-Chlorobenzaldehyde	p-Chloro chromene	82–91	235–240
4-Nitrobenzaldehyde	p-Nitro chromene	75–85	245–250

VII. CHARACTERIZATION OF CHROMENE DERIVATIVES

UV–Visible Spectroscopy

UV–Visible spectroscopic analysis of the synthesized 2-amino-2-chromene derivatives showed characteristic absorption peaks corresponding to different electronic transitions within the conjugated heterocyclic system. Absorption bands observed at 220–230 nm were assigned to $\pi \rightarrow \pi^*$ transitions, while peaks in the range of 270–285 nm corresponded to conjugated $\pi \rightarrow \pi^*$ transitions. Additional absorption bands observed between 320–340 nm were attributed to $n \rightarrow \pi^*$ transitions associated with the heterocyclic chromene framework. These spectral features confirmed the presence of a conjugated chromene system and indicated successful heterocyclic ring formation.

FTIR Analysis

FTIR spectroscopic analysis confirmed the formation of 2-amino-2-chromene derivatives through characteristic functional group vibrations. The broad absorption bands observed in the range of 3400–3320 cm^{-1} corresponded to NH_2 stretching vibrations, indicating the presence of amino functionality. Peaks observed between 1620–1580 cm^{-1} were assigned to C=C stretching vibrations of the aromatic and conjugated system, while absorption bands in the range of 1260–1220 cm^{-1} corresponded to C–O–C stretching vibrations of the chromene ether linkage. These spectral observations confirmed successful chromene ring formation and the presence of amino and ether functional groups in the synthesized compounds.

^1H NMR Analysis

The ^1H NMR spectra of the synthesized chromene derivatives exhibited characteristic signals corresponding to the chromene nucleus. Signals observed in the range of δ 4.8–5.2 ppm were assigned to the methine proton of the chromene ring, while aromatic proton signals appeared between δ 6.5–7.8 ppm. Additional signals observed at δ 7.8–8.2 ppm corresponded to NH_2 protons. These spectral characteristics confirmed the successful formation of the 2-amino-2-chromene framework and amino functionality.



¹³C NMR Analysis

The ¹³C NMR spectra further confirmed the structural framework of the synthesized chromene derivatives. Signals observed between δ 35–40 ppm were assigned to methine carbon atoms, while peaks in the range of δ 55–65 ppm corresponded to oxygen-bearing carbon atoms present in the chromene ring. Aromatic carbon signals appeared between δ 115–130 ppm, and oxygenated aromatic carbons were observed in the range of δ 145–160 ppm. These spectral observations confirmed the chromene carbon framework and successful cyclization during the multicomponent reaction.

VIII. RESULTS AND DISCUSSION

The synthesized cobalt oxide nanoparticles exhibited excellent catalytic performance in the one-pot multicomponent synthesis of 2-amino-2-chromene derivatives. The nanocatalysts provided high catalytic efficiency, shorter reaction times, improved selectivity, and excellent product yields under mild reaction conditions. The effect of substituents on the aromatic aldehydes was also investigated. Electron-donating groups such as $-\text{CH}_3$ and $-\text{OCH}_3$ increased the reaction rate and improved product yield, whereas electron-withdrawing groups such as $-\text{NO}_2$ and $-\text{Cl}$ slightly increased the reaction time but still provided products with good purity.

The developed synthetic methodology offered several advantages including one-pot synthesis, eco-friendly reaction conditions, recyclable catalyst system, reduced solvent usage, lower energy consumption, and high atom economy. These advantages make the process environmentally sustainable and economically beneficial compared to conventional synthetic methods.

Conclusion

The present study successfully demonstrated the green synthesis of cobalt oxide nanoparticles through an environmentally friendly method. Characterization studies using spectroscopic and analytical techniques confirmed the formation of nanoscale crystalline Co_3O_4 nanoparticles. The synthesized nanoparticles acted as efficient heterogeneous catalysts for the synthesis of 2-amino-2-chromene derivatives through a one-pot multicomponent reaction. The developed methodology provided high product yields, shorter reaction times, mild reaction conditions, and improved environmental sustainability. Spectroscopic characterization further confirmed the successful formation of the synthesized chromene derivatives. Overall, the present work represents an important advancement in green organic synthesis, nanocatalysis, and sustainable heterocyclic chemistry.

Future Scope

Future research in this area may focus on biological activity studies of the synthesized chromene derivatives, including anticancer evaluation and antimicrobial screening. Further investigations may also emphasize catalyst recyclability optimization, enhancement of catalytic efficiency, and industrial-scale green synthesis of cobalt oxide nanoparticles and chromene derivatives for pharmaceutical and environmental applications.

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