

ONE-POT SYNTHESIS OF SUBSTITUTED CHROMENE DERIVATIVES USING MgO NANOPARTICLES

Submitted in partial fulfilment of the requirements for the award of
Bachelor of Science Degree in Chemistry

By

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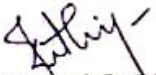
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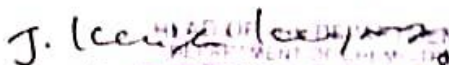
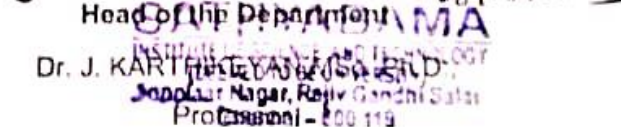
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BONAFIDE CERTIFICATE

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We **BALASANTHOSH.K AND VASANTHA KUMAR.V.E**, hereby declare that the Project Report entitled “**ONE-POT SYNTHESIS OF SUBSTITUTED CHROMENE DERIVATIVES USING MgO NANOPARTICLES**” done by me under the guidance of Dr. T. Krithiga M.Sc., M. Phil, Ph.D., Associate Professor, Department of Chemistry, Sathyabama Institute of Science and Technology is submitted in partial fulfilment of the requirements for the award of Master of Science degree in Chemistry

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ABSTRACT

Magnesium oxide nanoparticles have been synthesized by so-gel method as a reducing agent and magnesium nitrate as a starting material. The synthesized nanoparticle has been characterized by FTIR, XRD and SEM with EDAX. XRD studies show that Magnesium oxide nanoparticle as hexagonal wurtzite structure. The SEM analysis confirms the formation of spherical particles which are agglomerated. FTIR confirms the presence of Zn – O stretching bond. EDAX confirms the presence of Zinc and oxygen in the formed catalyst. The synthesized magnesium oxide nanoparticle was used as a catalyst for one pot synthesis of substituted chromene derivatives. These chromene derivatives were synthesized by one- pot two component condensation of vanillin (Aldehyde) and 4-hydroxy coumarin using Magnesium oxide nanoparticle catalyst in water under reflux condition. The synthesized product was characterized by FTIR and NMR spectroscopy techniques. The functional groups present in the product and its structure was confirmed by the spectral studies. A mechanistic approach for the formation of the product was proposed. A good product yield was obtained 65-70% with Magnesium oxide nanoparticle within practical time and ambient temperature.

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LIST OF ABBREVIATIONS

NMR	- Nuclear Magnetic Resonance Spectroscopy
FTIR	- Fourier Transform Infrared Spectroscopy
SEM	- Scanning Electron Microscope
XRD	- X-Ray Diffraction
EDAX	- Energy Dispersive X-Ray Analysis ¹²

CHAPTER 1

INTRODUCTION

1.1 HYDROXY COUMARIN

4-hydroxy coumarin is a hydroxyl coumarin that is coumarin in which the hydrogen at position 4 is replaced by hydroxyl group. 4-Hydroxy coumarin derivatives are principal starting material in the area of organic synthesis. Coumarin have multiple biological activities including disease prevention growth modulation and antioxidant properties. Coumarin have been synthesized by several routes including Pechmann, Perkin, Knoevenagel, Reformatsky and Wittig reaction. Coumarin appears as colourless crystals, flakes or colourless to white powder with a pleasant fragrant vanilla odour and bitter aromatic burning taste. They are readily soluble in ethanol, methanol, acetone, DMF, DMSO and water. Coumarin derivatives have received attention because of their biological and numerous pharmacological activities. Coumarin and its derivatives are widely used as additives to foods cosmetics and optical brightening agents. 4-Hydroxy coumarin derivatives in water- ethanol solvent combine under microwave irradiation and conventional method. It has special biological activities. These derivatives have amazingly broad spectrum of pharmacological and physical activities. These are important class of heterocyclic compounds which are widely occupied in many natural products. They are employed as the anticoagulant, antibacterial, antifungal, antiviral, antitumor, antiprotozoal, insecticidal, antimycobacterial, antimutagenic, antioxidant, anti inflammatory agents, HIV

protease inhibitors and tyrosinekinase inhibitors.(Khalil Tabaeiant et al.,2011).

1.2 MAGNESIUM OXIDE CATALYST

Researchers normally consider MgO as a promising high-surface-area heterogeneous catalyst support, additive, and promoter for many kinds of chemical reactions due to its certain properties, including stoichiometry and composition, cation valence, redox properties, acid-base character, and crystal and electronic structure. The presence of MgO as a support catalyst also modifies the electronic state of the overall catalytic performance by electron transfer between the native catalyst and MgO as support. The influence is clarified by alteration of acid-base properties of the catalyst-supported MgO. Meanwhile, the method, chemical composition, and condition in the preparation of MgO are the important factors affecting its surface and catalytic properties. Therefore, MgO with a high surface area and nanocrystalline structure has encouraging applications for some reactions, including as dry reforming, dehydrohalogenation, oxidative dehydrogenation of butane, nanooxidative dehydrogenation of ethylbenzene, decomposition of CCl₄, oxidative coupling of methane, hydrodesulfurization reactions, methane dimerization, and water gas shift reaction oxidation of CO by O₂ and ISO-propane conversion. This review highlights the synthesis and the role of MgO as a support catalyst and focuses on the design of better selective, energy-saving, durable, intrinsically clean, and safer catalytic processes.

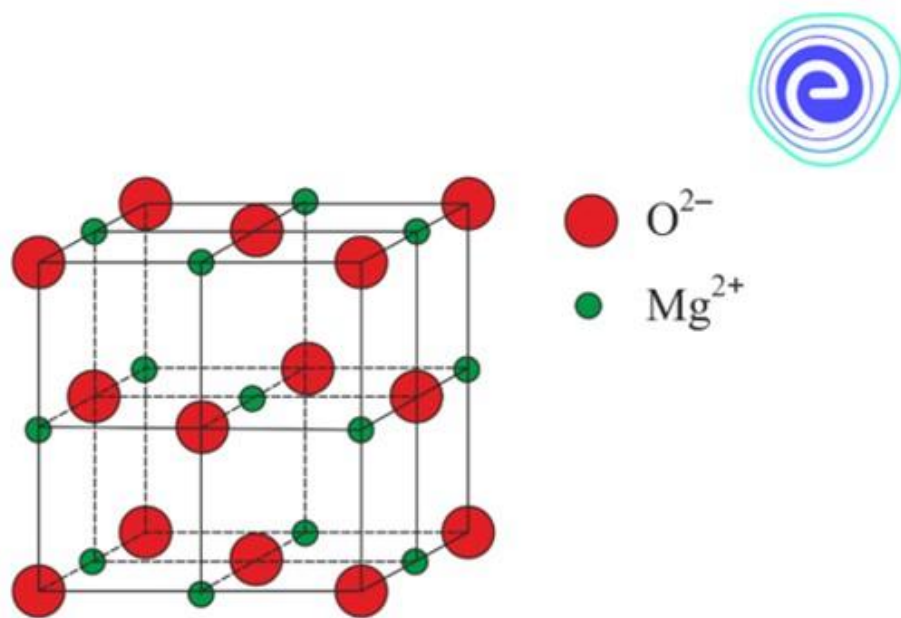


Fig 1.1 Magnesium Oxide structure

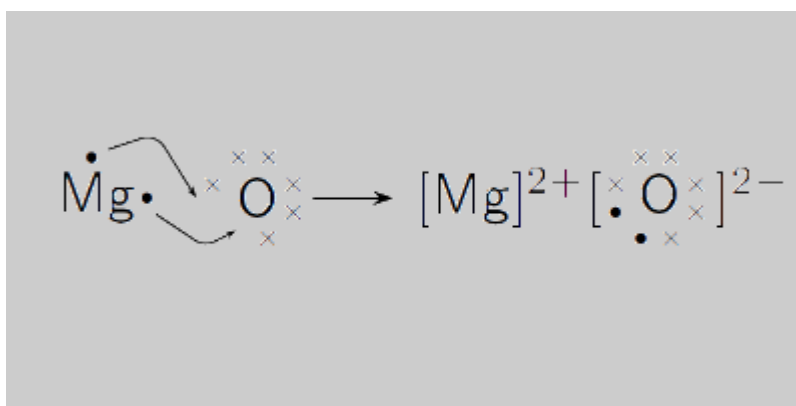


Fig 1.2 Magnesium oxide catalyst

CHAPTER 2

LITERATURE SURVEY

In recent years, Multicomponent condensation reaction involving a three or more reactants in one pot synthesizes a structurally diverse bioactive heterocyclic compound. The synthetic schemes are designed in such a way that there is very least pollution to the environment. In a typical experiment, aromatic aldehyde, secondary amine, 4- hydroxy coumarin and alum catalyst are used to obtain a good yield and to reduce the environment pollution. A few related works are given below.

Ali Aminkhani et al done a remarkably efficient three-component reaction to synthesize 2-amino-4*H*-chromenes derivatives from malononitrile, various aromatic aldehydes, and orcinol was described at room temperature in CH₂Cl₂ in the presence of catalytic amount of triethylamine. (15 April 2019)
Journal of Heterocyclic Chemistry

Arjun V et al has done the synthesis of 2-amino-2-chromenes under solvent-free conditions is disclosed here using a silica triflate catalyzed one-pot three component condensation. This procedure stands out for its wide substrate scope, reduced reaction time, great yield, functional group compatibility, operational simplicity, and outstanding catalyst recyclability. (04 Feb 2022) Volume 43. Journal of polycyclic Aromatic Compounds

Chihe Mhiri et al has discussed Three-component reaction of arylaldehydes with malononitrile and 4-hydroxycoumarine using CH₃COONH₄ as a catalyst at reflux was used for the synthesis of novel substituted pyrano[3,2-

c]chromene derivatives. (19 November 2019). Journal of Heterocyclic Chemistry. (17 August 2021) Vol.3. Journal of Microbial Sciences

DeepanshuMonga discussed Environmental pollutants dyes, pesticides, pharmaceuticals, explosive waste and polyaromatic hydrocarbons. Environmental pollutants toxicity possible microbial biodegradation pathways of environmental pollutants. (17 August 2021) Vol.3. Journal of Microbial Sciences

Mohamed Khodja et al has discussed in Oil-Based drilling fluid systems (OBM, for Oil-Based Mud) the oil phase is the major source of contamination and hydrocarbon pollution is by far, the main concern. (7 March 2021) Vol.8 Journal of Cleaner Engineering and Technology

Mohammad Hossein et al in this research, GO/Fe₃O₄/UiO-66-NH₂, a new magnetically recoverable heterogeneous catalyst, was prepared and characterized using various spectroscopic techniques and elemental analysis methods. (5 September 2022) .Vol.1283

Manoj Pudukudy et al in this method a single pot sol-gel method was adopted for the synthesis of MgO nanoparticles supported nickel and iron catalysts for undiluted methane decomposition into CO_x free hydrogen and nanocarbon for the first time. The catalysts were successfully synthesized via a facile sol-gel route without the assistance of any surfactants. 5 December 2017. Vol.218. Journal of Molecular Structure

Nikita Dhiman et al has discussed the degradation behavior in the vicinity of different parameters like pH, biomass, concentration and temperature was investigated. (30 July 2021) Vol.25

Sejal P. Dalal et al has done the study, the waste PB were grinded and used as replacement of fine aggregate (sand) at substitution levels of 5%, 10%, 15%, 20%, 25% and 30% by weight of sand per cubic meter of concrete. The compressive, flexural, and tensile strength as well as the water absorption of concrete mixes was investigated. (16 December 2021) Vol. 14

Xiaogang Zheng et al You Sandwich-like MgO/Carbon (MgO/C) Nano composites were fabricated using a one-pot hydrothermal route for the removal of organic dyes. The effects of contact time, pH value, carbon thickness, inorganic ions, and temperature on the sorption capacity of MgO@C were investigated. Further investigation indicated that the sorption process of methyl orange over sandwich-like MgO@C was controlled by the external mass transfer and intraparticle diffusion, and was a spontaneous and exothermic adsorption process. (15 February 2018) Vol.334

CHAPTER 3

AIM AND SCOPE

3.1 AIM

The main aim of this project is to synthesize ZnO nanoparticle. The synthesized catalyst catalytic activity is tested by one pot synthesis of 4-hydroxy coumarin and vanillin to form chromene derivatives

3.2 SCOPE

- Synthesizing MgO nanoparticle using MgNO_3 and NaOH
- Characterization of synthesized MgO nanoparticle by FT-IR spectroscopy, XRD, SEM and EDX
- Preparation of chromene derivatives using synthesized MgO nanoparticle
- Confirmation of product formed by characterizing by FT-IR, ^1H -NMR, ^{13}C -NMR Spectroscopy

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIALS

Materials used in this reaction are zinc acetate dihydrate, sodium hydroxide, deionised water, 4-hydroxy Coumarin and Vanillin which were purchased from Merck chemicals and used as such without further purification. Thin-layer chromatography (TLC) analysis was performed with TLC silica gel 60 F₂₅₄ obtained from Merck.

4.2 CHARACTERIZATION TECHNIQUES

4.2.1 Fourier Transform Infrared Spectroscopy

FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time. Spectroscopy is the study of interaction of electromagnetic waves (EM) with matter. The surface functional groups of the samples were qualitatively analyzed by FTIR spectroscopy (Bruker FTIR) and recorded in the range of 4000 – 600 cm⁻¹. For this purpose, the samples were mixed with potassium bromide and made into pellets for analysis.



Fig 4.1 Fourier Transform Infrared Spectroscopy

4.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectroscopy most commonly known as NMR spectroscopy or magnetic resonance spectroscopy (MRS) is a spectroscopic technique to observe local magnetic fields around atomic nuclei. The sample is placed in a magnetic field and the NMR signal is produced by excitation of the nuclei sample with radio wave into nuclear magnetic resonance, which is detected with sensitive radio receivers. The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule and its individual functional groups. As the fields are unique or highly characteristic to individual compounds, in modern organic chemistry practice, NMR spectroscopy is the definitive method to identify monomolecular organic compounds. Similarly biochemists use NMR to identify proteins and other complex molecules.



Fig 4.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

Besides identification, NMR spectroscopy provides detailed information about the structure, dynamics, reaction state, and chemical environment of molecules. The most common type of NMR are proton and carbon-13 NMR spectroscopy, but it is applicable to any kind of sample that contains nuclei possessing spin. The detailed structural information where qualitatively analyzed by NMR spectroscopy (Bruker Advance III 500 MHz). Solvent used in this method is CDCl_3 **Resonance Magnetic Spectrometer**.

4.2.3 Powder X-Ray Diffraction (XRD)

The powder X-Ray diffraction (XRD) is a logical spectroscopic strategy utilizing Xbeam, neutron and electron diffraction on powder or microcrystalline examples. This spectroscopic method is utilized to recognize the nuclear just as sub-atomic structure of precious stone. In this spectroscopic method the estimation of gem is mounted on a goniometer and it bit by bit pivoted. After this procedure is shelled with X-beams to create

a diffraction example of consistently divided spots known as reflections. The points and forces of these diffracted shafts, the crystallographer creates three dimensional pictures of the precious stone. The X-beam diffraction strategy likewise used to separate the idea of crystalline materials from nanocrystalline materials and the structure recognizable proof is produced using the x-beam diffraction design examination. This XRD design contrast it and the universally perceived by database containing the reference design (JCPDS) card. In XRD pattern the average crystalline size of nanomaterial derived from the following Scherrer formula:

$$\text{Scherrer equation} = (D = K\lambda/\beta\cos\theta)$$

Where, K = e shape factor (0.9)

λ = wavelength of X-rays, β =
corrected full width at half-
maximum; θ = angle of peak

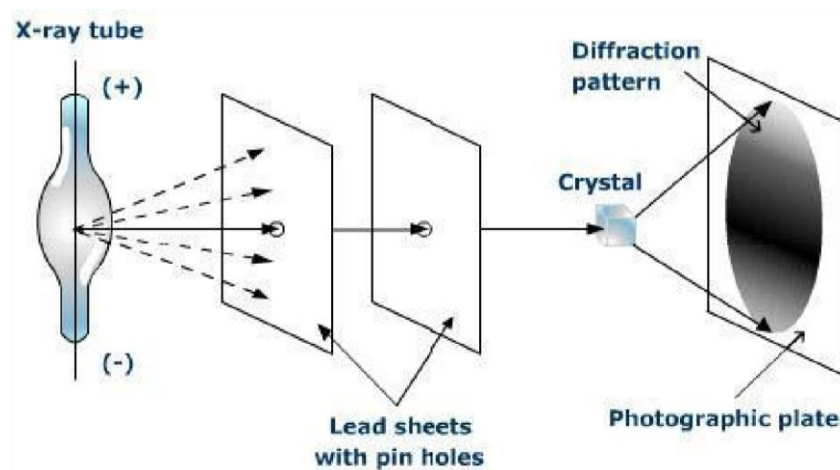


Fig 4.3 Power X-Ray Diffraction

4.2.4 Scanning Electron Microscopy

The scanning electron microscopy is vital sorts of portrayal procedure and it utilizes an engaged electron bar and to check strong example from the optical to the nanoscale run. In these kinds of portrayal procedures, auxiliary electrons are transmitted from the example and it gathered to make a region guide of the optional discharge. The force of auxiliary outflow is relies upon neighbourhood morphology. In SEM examination systems electron bar goes through the thin example since it is exceptionally arranged thin example are upheld on the TEM matrix. In this strategies picture appeared fluorescent screen and picture is a two dimensional projection of test. They give three dimensional pictures and it has 0.4 nanometer in size. The SEM depends on dispersed electrons and dissipated electrons in SEM strategies created picture of the example after magnifying instrument gather and checks dissipated electrons. It offers 2 million greatest dimension of amplification. The scanning electron microscopy is utilized to decide the outer morphology (surface), concoction arrangement and crystalline structure of the nanomaterials tests. In SEM examination systems the zones territory from around 1 cm to 5 microns in width can be imaged in a filtering mode utilizing unsurprising SEM methods and having amplification run from spatial goals of 50 nm to 100 nm. The different frequencies are utilized for the goals of tests and it gives different morphological shapes pole, package and bloom to the concerned nanomaterial. The gadget and capacity of the SEM is fundamentally the same as the electron test microanalyser (EPMA) and noteworthy covers in ability exist between the two instruments.

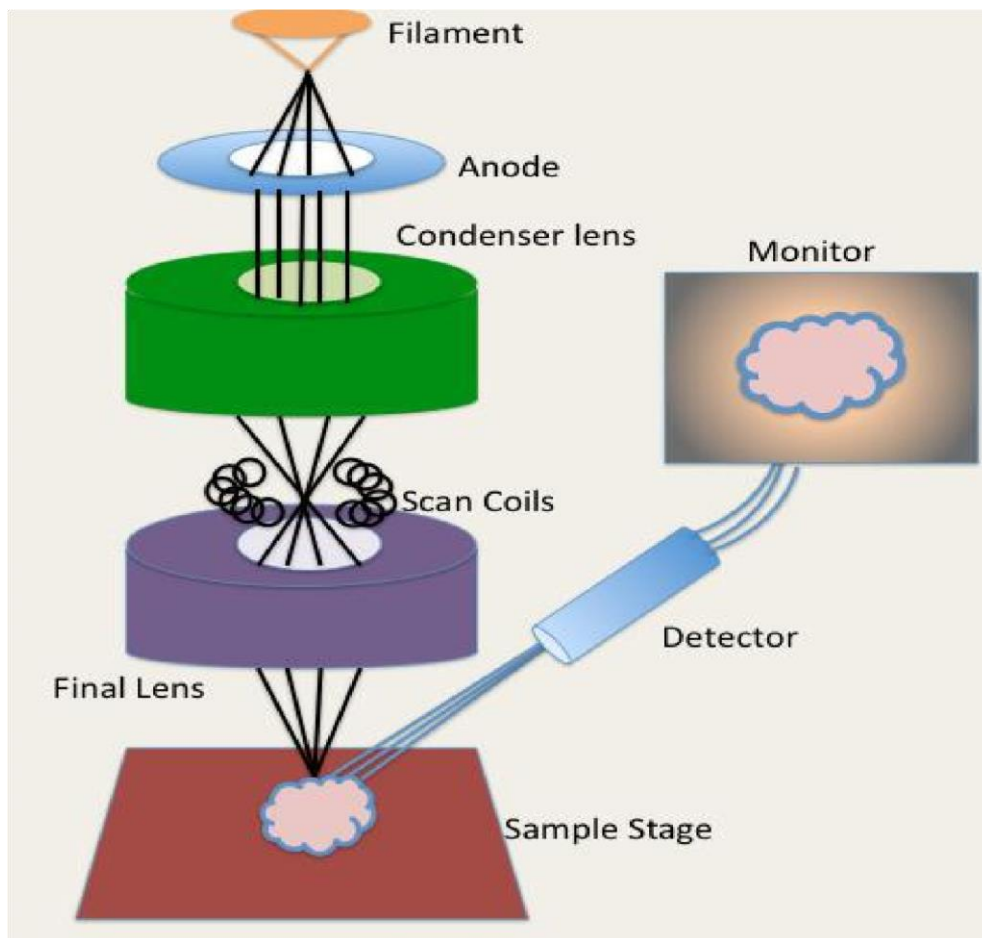


Fig 4.4 Scanning Electron Microscope

4.3 SYNTHESIS OF MgO NANOPARTICLE

4.3.1 Preparation of Zinc Oxide Nanoparticles

- 0.1M of NaOH is prepared by dissolving 0.300g of NaOH in 100ml distilled water. Take 40ml of prepared NaOH solution in a beaker and place it in hot

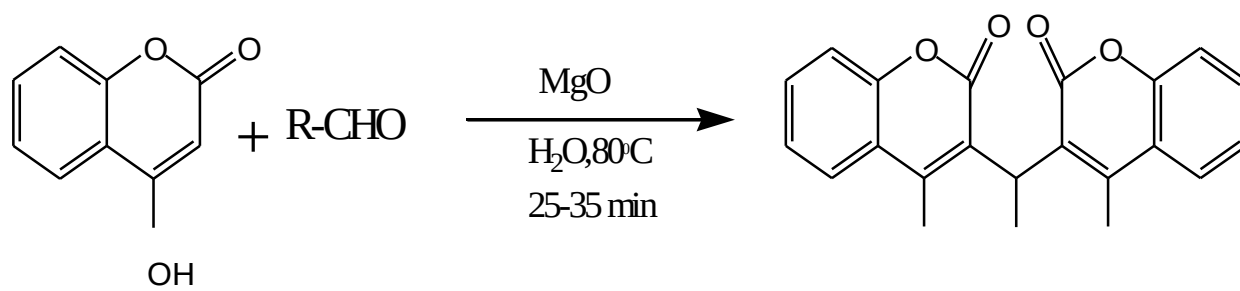
plated magnetic stirrer when the solution gets boiled then MgNO₃ is added drop by drop (mag stirrer 30C).

- A gel like consistency is formed turn off the stirrer and transfers it to a crucible. Place the crucible in oven for (80C)° the moisture to evaporate (approximately 3hrs). Then filter it, wash it, and dry it. And then weight it.

4.4 ONE POT SYNTHESIS

4.4.1 Synthesis of 3, 3' - ((3 – Hydroxy – 4 – Methoxyphenyl) Methylene) bis (4-Hydroxy-2H-Chromene-2-One)

The reaction is simply carried out by mixing 4-hydroxy coumarin, vanillin in the ratio of 1:2 and the catalyst MgO nanoparticle was added and water is used as a solvent. The effect of catalyst and different solvents such as ethanol and chloroform on the yield of product was evaluated. The yield of the product was 70%. The product formation and yield was better in water solvent. The product formed was characterized by FTIR and ¹H NMR and ¹³C NMR Spectroscopy studies



4-Hydroxy coumarin Aldehyde

Fig 4.5 Reaction scheme of formation of substituted chromene derivative

CHAPTER 5

RESULT AND DISCUSSION

5.1 CHARACTERIZATION OF ZINC OXIDE NANOPARTICLES

5.1.1 FTIR Spectrum Zinc oxide nano particles

The FT-IR spectrum of Magnesium Oxide nanoparticles is shown in the IR vibrational frequencies obtained at 3387 cm^{-1} , 1636 cm^{-1} , 1499 cm^{-1} , 1400 cm^{-1} and 539 cm^{-1} correspond to O-H stretching of adsorbable water molecule on zinc oxide, C=O stretching, water and CO_2 molecule adsorption on MgO surface, O-H in-plane bending of carboxyl group adsorbed on MgO and metal – oxygen bond Mg-O stretching respectively. The peak at 539 cm^{-1} is the characteristic peak for MgO nanoparticle.

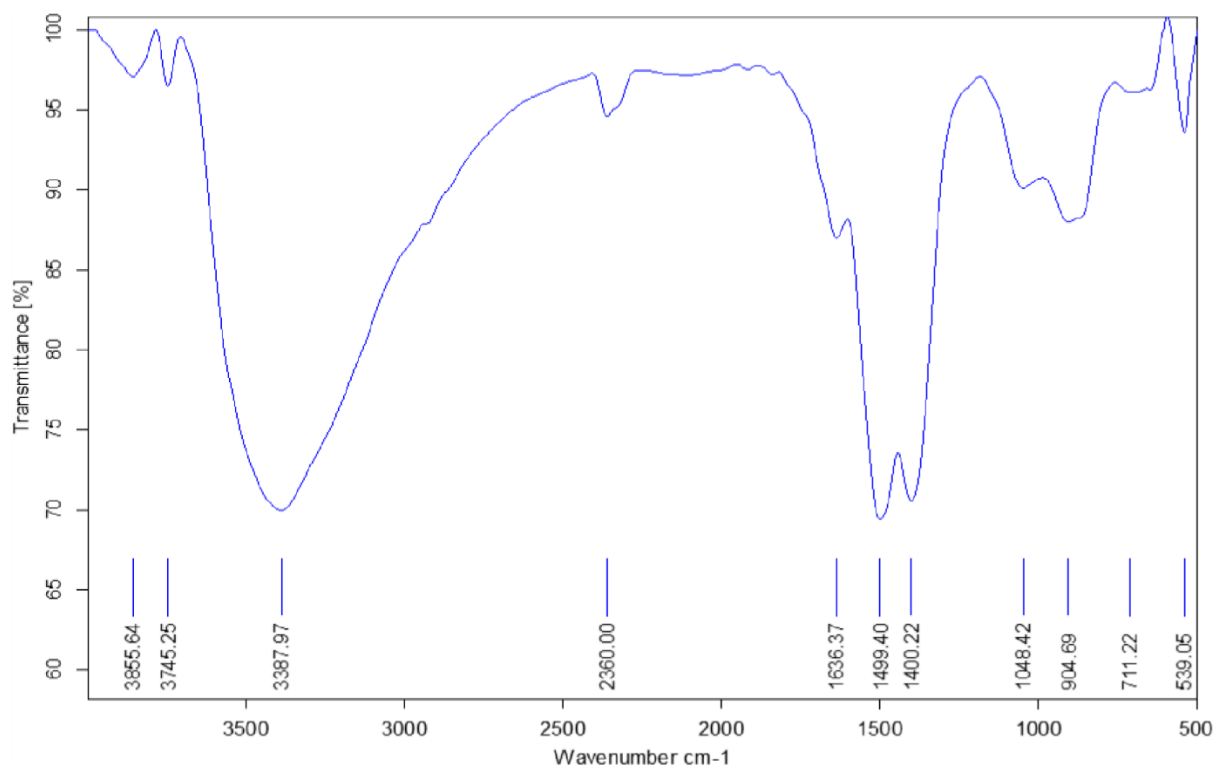


Fig 5.1 FTIR spectrum of Magnesium Oxide Nanoparticle

Table 5.1 Vibrational frequencies of MgO Nanoparticle in FTIR Spectra

Vibrational frequency	Functional group identification
3387 cm^{-1}	O-H stretching of adsorbable water molecule on zinc oxide
2360 cm^{-1}	C=O stretching
1636 cm^{-1}	Water and CO ₂ molecule adsorption on MgO surface
1499 cm^{-1}	Water and CO ₂ molecule adsorption on MgO surface
1400 cm^{-1}	O-H in-plane bending Asymmetric stretching of carboxyl group on MgO
539 cm^{-1}	Mg-O stretching

5.1.2 SEM with EDAX image of Magnesium oxide Nanoparticle

The SEM image of Zinc oxide nanoparticles is shown in the Fig. 5.2. The image depicts that Zinc oxide nanoparticle obtained have spherical shape. The SEM image also shows the presence of agglomerates of ZnO nanoparticles. The EDAX image of Zinc Oxide nanoparticle is shown in the Fig. 5.3. The EDAX spectra shows the presence of Zn and O in the ZnO catalyst.

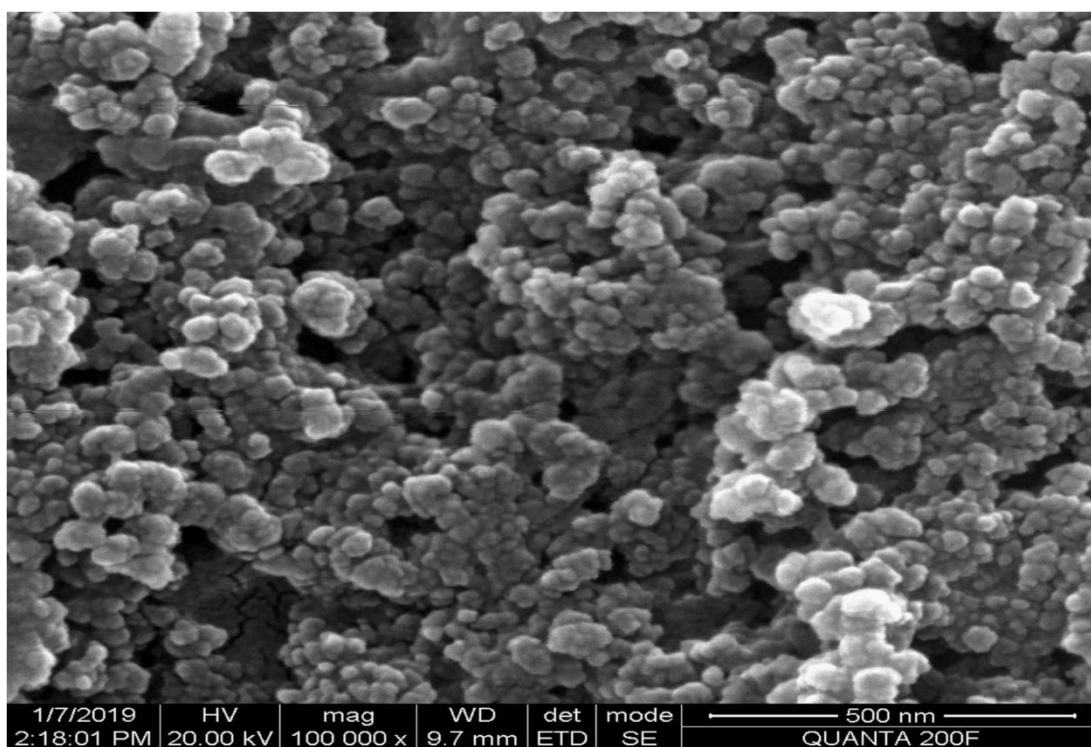


Fig 5.2 SEM image of Magnesium oxide nanoparticles

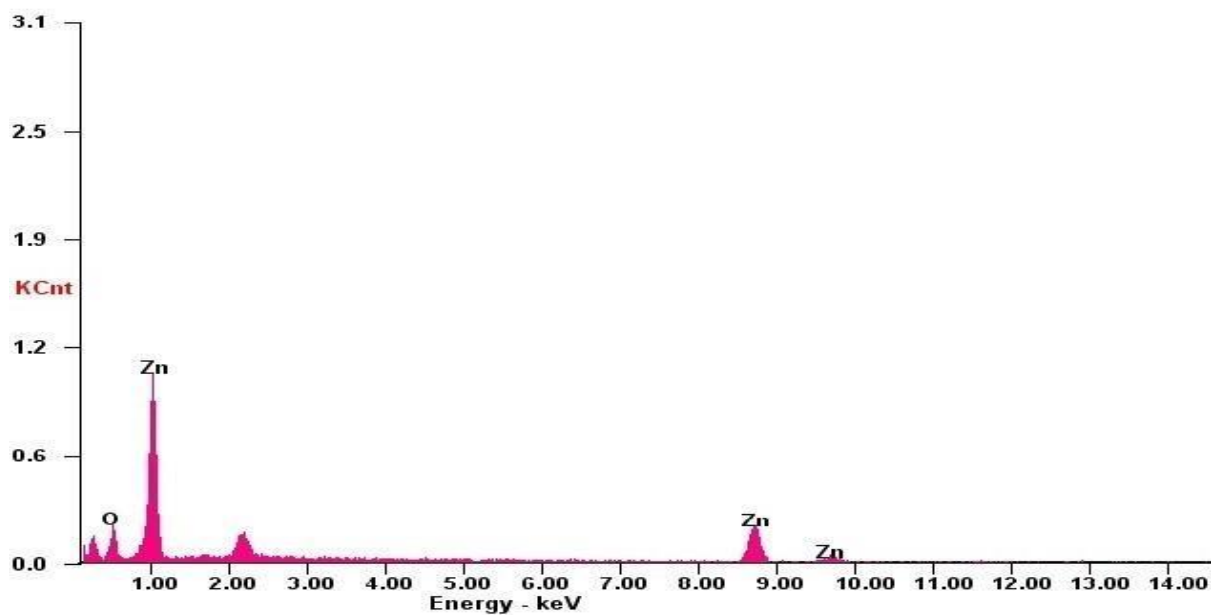


Fig 5.3 EDAX Image of Magnesium Oxide nanoparticles

5.1.3 XRD Pattern of Magnesium Oxide Nanoparticles

The XRD pattern of Magnesium oxide nanoparticles is shown in the Fig. 5.4. X-ray diffraction was carried out to confirm the hexagonal wurtzite phase of zinc oxide nanoparticles. The peaks at 2θ values of 31.78° , 34.41° , 36.26° , 47.59° , 56.59° , 62.80° , 65.84° , 6.96° , 68.30° , 72.12° and 76.53° corresponds to the hexagonal phase of (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) of zinc oxide nanoparticles.

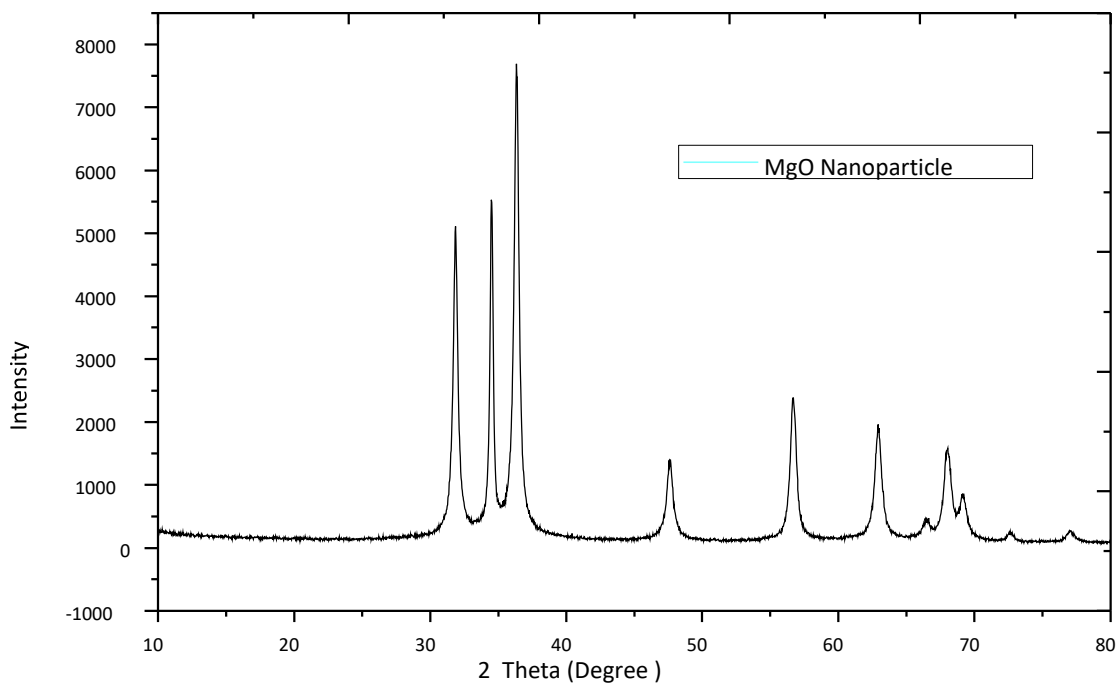


Fig 5.4 XRD Pattern of Magnesium oxide Nanoparticle

5.2 SYNTHESIS OF 3, 3' - ((3 – HYDROXY – 4 – METHOXYPHENYL) METHYLENE) BIS (4-HYDROXY-2H-CHROMENE-2-ONE)

The reaction is simply carried out by mixing 4-hydroxy coumarin, vanillin in the ratio of 1:2 and the catalyst ZnO nanoparticle was added and water is used as a solvent. The effect of catalyst and different solvents such as ethanol and chloroform on the yield of product was evaluated. The yield of the product was 70%. The product formation and yield was better in water solvent. The product formed was characterized by FTIR and ¹H NMR and ¹³C NMR Spectroscopy studies.(Renata Gasparova et al .,2009).

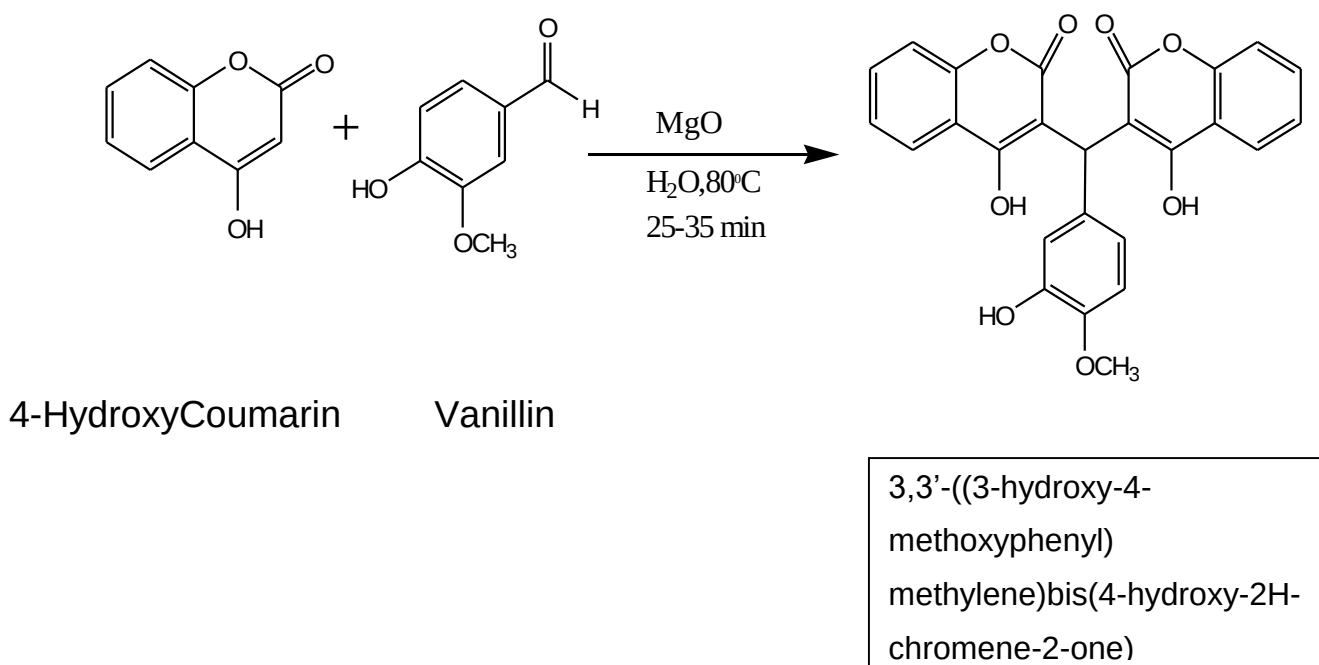


Fig 5.5 Reaction scheme for the formation of 3, 3' - ((3 – Hydroxy – 4 – Methoxyphenyl) Methylene) bis (4-Hydroxy-2H-Chromene-2-One)

5.2.1 Spectral Data of 3, 3' - ((3 – Hydroxy – 4 – Methoxyphenyl) Methylene) bis (4-Hydroxy-2H-Chromene-2-One)

FTIR Data: The FTIR spectra of the product is given the Fig. 5.6. The product peaks are 3494 cm^{-1} , 3073 cm^{-1} , 2727 cm^{-1} , 1095 cm^{-1} which corresponds to O-H, C-H Stretch, CHO linkage, C=O Stretch.

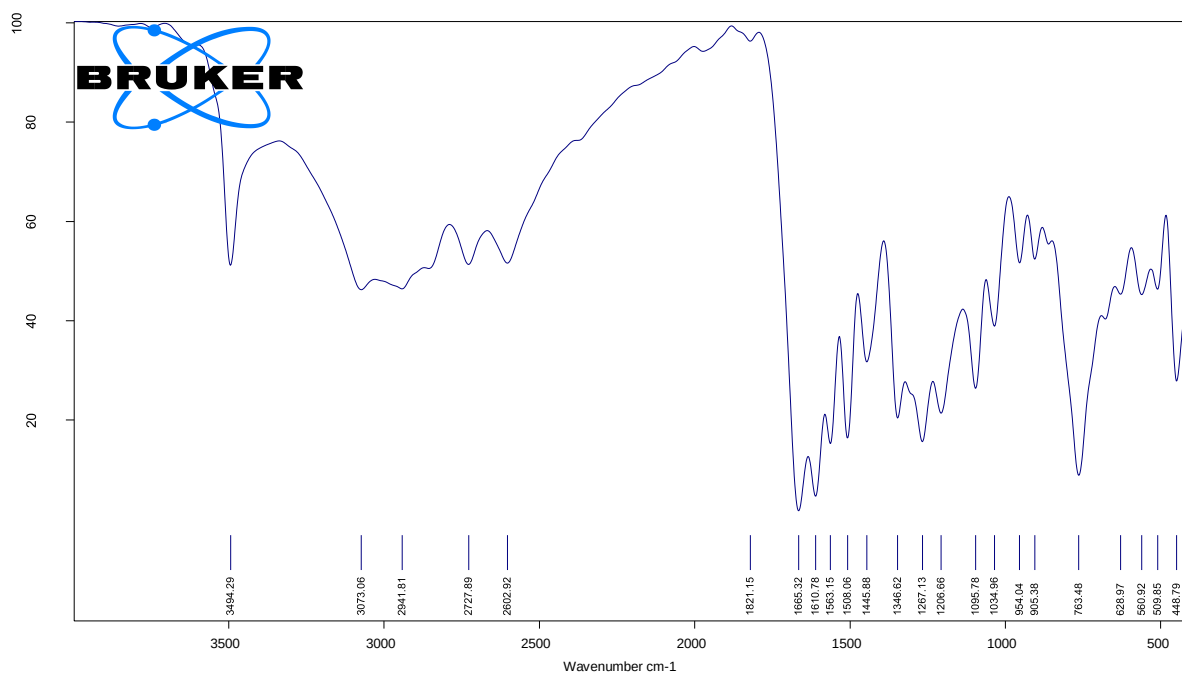


Fig 5.6 FTIR spectra of 3, 3' - ((3 – Hydroxy – 4 – Methoxyphenyl) Methylene) bis (4-Hydroxy-2H-Chromene-2-One)

Table 5.2 Vibrational frequencies of 3, 3' - ((3 – Hydroxy – Methoxyphenyl) Methylene) bis (4-Hydroxy-2H-Chromene-2-One) in FTIR spectra

Vibrational frequency	Functional group identification
3494	O-H stretching
3073	C-H stretching
2727	C-H-O linkage
1346	O-H bending
1267	C=O stretching
763	Meta substitution
560	ZnOnano

NMR Data: The ^1H NMR and ^{13}C NMR spectra of the 3, 3' - ((3 – hydroxy – 4 – methoxyphenyl) methylene) bis (4-hydroxy-2h-chromene-2-one) are given in the Fig. 5.7 and 5.8 which confirm its structure. The Table 5.3 shows the *Chemical shift of structural units in 3, 3' - ((3 – Hydroxy – 4 – Methoxyphenyl) Methylene) bis (4Hydroxy-2H-Chromene-2-One)* from ^1H NMR Spectrum.

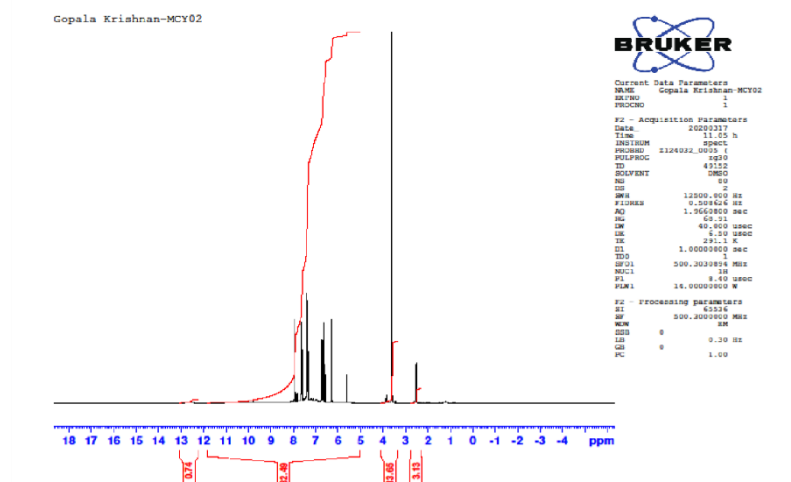


Fig. 5.7 ^1H NMR Spectra of 3, 3' - ((3 – Hydroxy – 4 – Methoxyphenyl) Methylene) bis (4-Hydroxy-2H-Chromene-2-One)

Table 5.3 NMR Spectra of 3, 3' - ((3 – Hydroxy – 4 – Methoxyphenyl) Methylene) bis (4-Hydroxy-2H-Chromene-2-One)

Chemical shift of structural units in 3, 3' - ((3 – Hydroxy – Methoxyphenyl) Methylene) bis (4-Hydroxy-2H-Chromene-2-One) from ^1H NMR Spectrum

Chemical shift(δ)	Structural unit
2.7	O-CH ₃
2.5	Aromatic Ester
3.5	O-H
5.5	Vinylic Proton
7.0-8.5	Aromatic Proton

CHAPTER 6

CONCLUSION

A simple, convenient and environmentally benign one-pot synthesis of 4-hydroxy coumarin derivatives using MgO nanoparticle catalysts have been developed. The one-pot, two component condensation of an aldehyde and 4-hydroxy coumarin gives an excellent yield (65 – 70%) of 4-hydroxy coumarin derivatives within a practical reaction time at ambient temperature. The effect of catalyst and different solvents such as water and ethanol on the yield of product was evaluated. The product formation and yield was better in ethanol solvent. The desired products can be also obtained in high yields and purities without further chromatographic purification. The simple experimental procedure, short reaction times, excellent yields of products, mild reaction condition, easy purification, economic availability of the catalyst, and green standard are the advantages of this method.

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