ACCEPTORLESS DEHYDROGENATIVE SYNTHESIS OF KETONES FROM ALCOHOLS USING CARBON SUPPORTED Ni NANO-CATALYST

M.Sc. THESIS

A

**DISSERTATION SUBMITTED IN PARTIAL
FULFILLMENT OF THE REQUIREMENT FOR
THE DEGREE OF**

MASTER OF SCIENCE (M.Sc.)

IN

CHEMISTRY

**SUBMITTED
BY
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SESSION: OCTOBER-2018
MAY, 2022**

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THESIS ACCEPTANCE LETTER

The thesis titled **"ACCEPTORLESS DEHYDROGENATIVE SYNTHESIS OF KETONES FROM ALCOHOLS USING CARBON SUPPORTED Ni NANO-CATALYST"** submitted by Samapti Singha Roy, Roll No.:1018032606, Registration No.: 1018032606, Session: October-2018 has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Master of Science (M.Sc.) in Chemistry on May16, 2022.

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CANDIDATES DECLARATION

It is hereby declared that this thesis/project or any part of it has not been submitted elsewhere for the award of any degree or diploma.

Samapti Singha Roy

Samapti Singha Roy

Dedicated to My Beloved Family

&

Honorable Supervisor

Acknowledgement

At the beginning, I humbly acknowledge my deepest gratitude to the Almighty, the most gracious, benevolent and merciful creator for His infinite mercy bestowed on me in carrying out the research work presented in the dissertation.

It is a great pleasure for me to acknowledge my deepest sense of gratitude, sincere, appreciation, heartfelt indebtedness and solemn regards to my reverend teacher and supervisor Dr. Md. Ayub Ali, Assistant Professor, Department of Chemistry, Bangladesh University of Engineering and Technology (BUET), for his kind supervision, indispensable guidance, valuable and constructive suggestions, liberal help and continuous encouragement during the whole period. It is obvious that his attributive contribution and efforts have greatly shaped me into what I am today. In fact, I am quite lucky to be a part of his ambitious research team.

It is my great honor to convey my sincere gratitude to my respected teacher Professor Dr. Md. Abdur Rashid, honorable Head of the Department of Chemistry, BUET for giving me his wonderful support to move through the academic processes during this M.Sc. program. I would like to convey my deepest gratitude to Professor Dr. Md. Wahab Khan for giving me an opportunity to use all instrument, apparatus from his laboratory.

I am thankful to all other respected teachers of the Department of Chemistry, BUET, for their continuous support. I would also like to thank all of the officers and staffs of the Department of Chemistry, BUET for their relentless help during my study period. My special thanks to Md. Moniruzzaman, Department of Chemistry, BUET, Dhaka for his cooperation in taking FT-IR spectrums.

I am highly thankful to Md. Jewel Hosen, scientific Officer, BCSIR, Dhaka and Md. Emdad Hossain, Scientist, WMSRC, Jahangirnagar University for characterizing of my samples.

I am grateful to Department of Glass and Ceramics Engineering, Bangladesh University of Engineering and Technology for the catalyst characterizations of XRD during my research.

I am highly grateful to all members of the board of examiners for their valuable suggestions and appreciated comments.

I am thankful to my dear consociate and all the members of Organic Synthesis and Catalysis Laboratory for their friendly cooperation and lovely encouragement throughout my research period. My special thanks to Md. Midul Islam, Asuthous Nath, M.M.A. Shofi Uddin Sarker, Sonjoy Das, Tohin Akter, Md. Kamruzzaman, Ifat nur dibbo,Rabeya Akter, Rafi ahmed and Md.Jamal Howlader for their continuous help during the research.

Finally, I would like to express my heartfelt indebtedness and profound gratitude to my beloved father, mother and all of my family members for their continuous inspiration and immeasurable sacrifices throughout the period of my study.

May 16, 2022 Samapti Singha Roy

Abstract

Ketones are one of the most indispensable organic moieties found in pharmaceuticals, agrochemicals, and other fine chemical industries. In this study, I have shown the successful example of a reusable catalyst for dehydrogenation of secondary alcohol by Ni/AC (Activated carbon) catalyst. At first nickel sulfate was taken in a beaker and dissolved in distilled water to prepare a nickel sulfate solution. After that, activated carbon was added to the solution, and the mixture was heated for 15 min at 80 ℃ with stirring. This mixture was evaporated with an evaporator and dried in an oven for 6 h at 90 ℃. The solid mixture was then calcined for 2 h at 400 ℃. The supported precursors were reduced in a two-necked reaction flask fitted with a reflux condenser, heated in a sand bath at 80 ℃ with continuous stirring in the presence of $N_2H_4.H_2O$ and NaOH solution to maintain the desired pH of 10-12. The mixture was filtered after reduction and rinsed with distilled water and 99 percent ethanol. To obtain the desired Ni/AC catalyst, then it was dried in an oven at 110°C for 6 hours. Following the previous procedure to prepare Ni/Al_2O_3, Ni/TiO_2, Ni/CeO_2, Ni/Nb_2O_5 &Ni catalyst.

Liquid phase chemical reduction method for Catalyst Preparation. In this method activated carbon was impregnated into $NiSO_4$ solution with vigorous stirring at room temperature for 1 h. Then the resulting suspension was heated at 80 ℃ and stirred for 30 min. Then the solution of N_2H_4. H_2O and NaOH were added to the suspension with stirring for 15 min. Then the filtration of the suspension and washed with distilled water with 99% ethanol. Then it was dried in an oven at 110 ℃ for 6 h to get the expected Ni/AC catalyst. Following the previous procedure to prepare Ni/Al_2O_3, Ni/TiO_2, Ni/CeO_2, Ni/Nb_2O_5 &Ni catalyst. Finally, it was characterized by several modern techniques such as scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Then the catalytic activity of the Ni/AC catalyst was checked by a model reaction. For the model reaction, 1-phenyl ethanol was mixed in a round bottom flask with the catalyst. Then the solvent was added to the reaction mixtures. Then the reaction mixture was heated in the presence of o-xylene reflux condition for 30 hrs. The progress of the reaction was monitored by thin layer chromatography (TLC) with an appropriate solvent ratio. Finally, completion of the reaction was confirmed by TLC. After completion of the reaction, the catalyst was separated from the reaction mixture by centrifugation, followed by washing with acetone, and dried at 100 ºC for 3h. The reusability was checked for the recovered catalyst. The product was purified by column chromatography. The synthesized pure ketone product was characterized by using FT-IR, ^1H NMR, ^{13}C NMR, and GC-MS.

In conclusion, a novel, versatile and sustainable method was developed for the synthesis of ketones from 1-phenyl ethanol using Ni/AC heterogeneous catalyst.

Keywords: ketone, Ni/AC Heterogeneous catalyst.

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Table

List of Abbreviation

Elaborations	Abbreviations
Broad singlet	**br s**
Mega Hertz	**MHz**
Hertz	**Hz**
Singlet	**s**
Doublet	**d**
Triplet	**t**
Quartet	**q**
Multiplet	**m**
Infrared Spectroscopy	**IR**
Nuclear Magnetic Resonance	**NMR**
Round bottomed flask	**RB**
Thin Layer Chromatography	**TLC**
Proton NMR	**^{1}H-NMR**
Carbon-13 NMR	**^{13}C-NMR**
Tetrahydrofuran	**THF**
Coupling constant	***J***
Tetramethyl silane	**TMS**
Deuterated chloroform	**$CDCl_3$**

Chapter -1
Introduction

1.1. Introduction to ketone

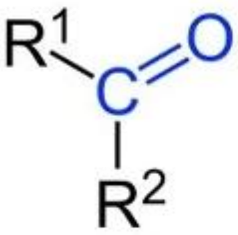


Fig. 1.1: Structure of ketone

Ketones are organic compounds containing carbonyl groups (C=O). ketones are characterized by the presence of a carbonyl group in which the carbon atom is covalently bonded to an oxygen atom. The remaining two bonds are to other carbon atoms or hydrocarbon radicals (R)[1].

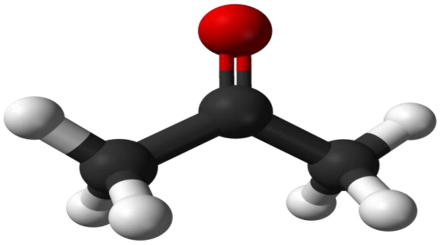
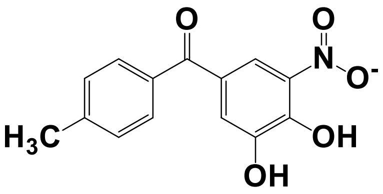


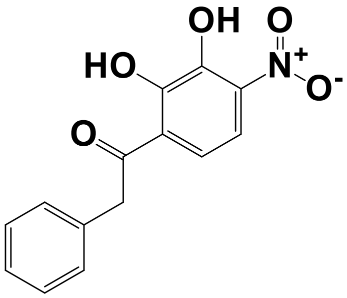
Fig..1.1: ketone bond formation

Ketones functional groups are important in natural and synthetic organic compounds. It is widely present in drugs, pharmaceuticals, natural products, and agrochemicals. Ketones are one of the most indispensable organic moieties found in pharmaceuticals, agrochemicals, and other fine chemical industries. In particular, acetophenone is used as a solvent in the manufacturing of plastics and resins [2].

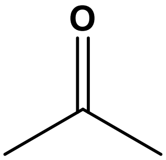
1.2. Importance of ketone



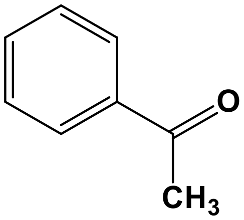
Tolcapone (a)



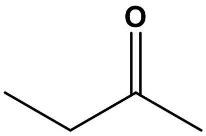
Nabumetone (b)



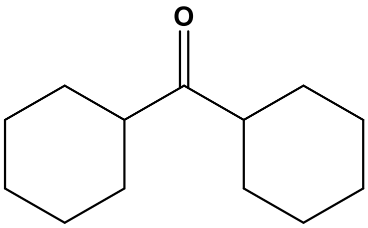
Acetone (c)



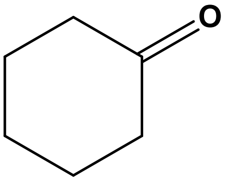
Acetophenone (d)



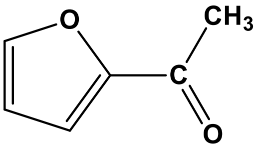
Butanone (d)



Dicyclohexyl ketone (e)



Cyclohexanone (f)



2-Furyl methyl ketone (g)

Heptanone(h) Octanone (i)

Figure. 1. 2: ketone bonds containing drug molecules (a-b), solvent products (c-e), Nylon production component (g), Agrochemicals (h), Biopesticide(i).

Acetone can be used as a paint thinner as well as a nail polish remover. It's also utilized for medical reasons, such as chemical peeling and acne treatments. One of the most prevalent solvents is butanone, often known as methyl ethyl ketone. It's used in the manufacture of textiles, varnishes, paint removers, paraffin wax, and plastics, among other things. Another major ketone is cyclohexanone, which is used in the manufacture of nylon. Acetophenone is a solvent used in the production of polymers and resins. As a biopesticide, heptanone, and octane are employed. As a fumigant, 2-fluryl methyl ketone is utilized. Dicyclohexyl ketone is used in organic synthesis reaction. Tolcapone and Nebumetone are also used as a drug [3-5].

1.3. Importance of ketone bond formation Reactions

In organic chemistry, the ketone bond is one of the most important and investigated reactions. Traditional ketone synthesis processes have a poor atom efficiency and a substantial volume of by-products with an unfavorable environmental character. One of the main difficulties in organic chemistry, according to the ACS Green Chemistry Institute and representatives of premier pharmaceutical businesses throughout the world, is ketone synthesis while avoiding poor atom economy reagent. Alternative reagents for ketone bond synthesis, which eliminate the use of poor atom economy chemicals, got nominations and were ranked first by all of the pharmaceutical companies in the survey, and were offered as a priority area [6].

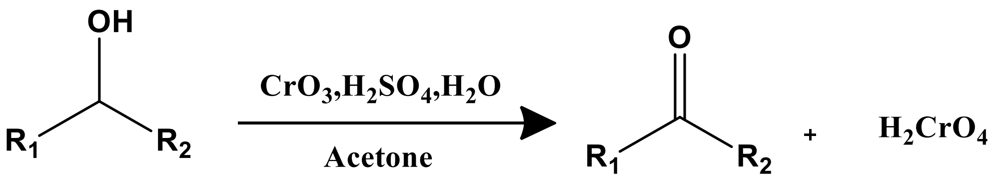
1.4. Synthesis of ketone

1.4.1. Conventional Methods

Oxidation Reaction:

Jones oxidation

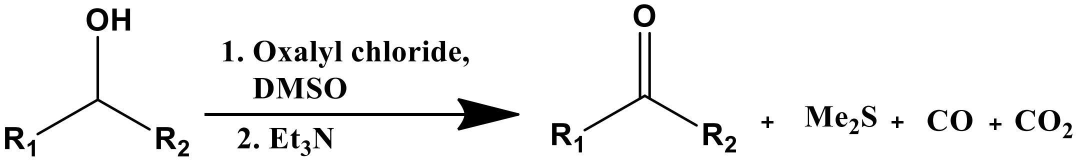
The Jones oxidation is an organic reaction that converts carboxylic acids and ketones from primary and secondary alcohols, respectively. A solution of chromium trioxide in aqueous sulfuric acid is known as Jones reagent. This acidic combination is then added to an acetone solution of the substrate to accomplish a Jones oxidation. Secondary alcohol treatment with the Jones reagent in the presence of acetone produces ketone and hazardous byproducts. These ketone bond forming reactions have some disadvantages, including as low atom efficiency and the production of a substantial amount of undesirable toxic byproducts [7].



Scheme 1.1: Jones oxidation for ketone-bond formation.

Swern oxidation

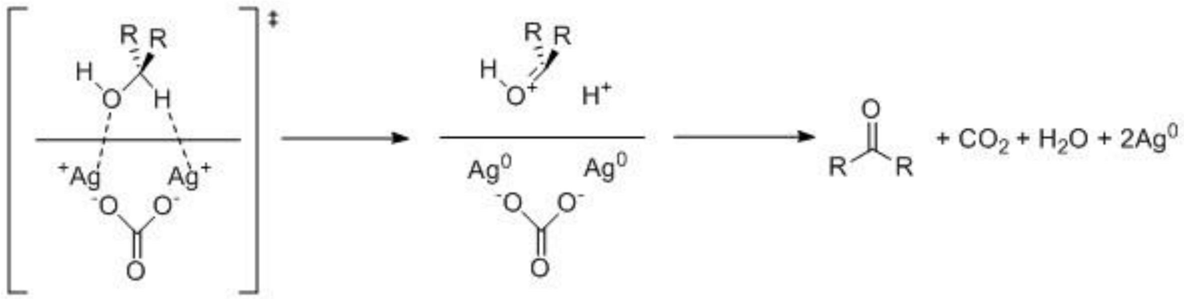
Swern oxidation uses oxalyl chloride and dimethyl sulfoxide to convert secondary alcohols to ketones. An organic base, such as triethylamine, is also required. Dimethyl sulfide (Me_2S), carbon monoxide (CO), carbon dioxide (CO_2), and triethylammonium chloride (when triethylamine is employed as a base) are the by-products ($C_6H_{15}NHCl$). Carbon monoxide and dimethyl sulfide are highly poisonous and odorous chemicals. These ketone bond formation reactions have certain disadvantages, such as low atom efficiency and the production of a substantial amount of undesirable toxic byproducts [8-11].



Scheme 1.2: Swern oxidation for ketone-bond formation.

Fetzion oxidation

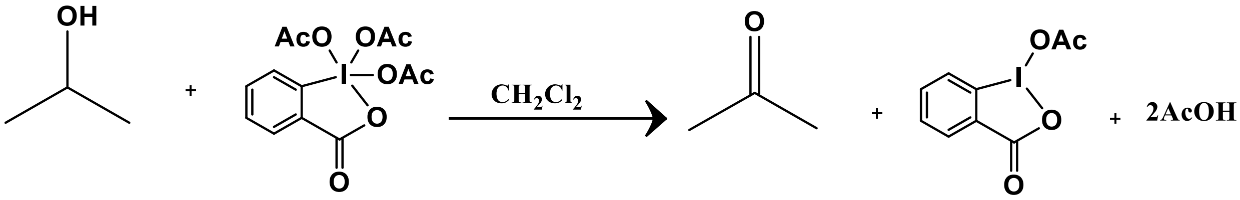
The oxidation of primary and secondary alcohols using silver (I) carbonate adsorbed into the surface of celite, commonly known as Fétizon's reagent, is known as Fétizon oxidation. It's a gentle reagent that can be used on acid and base-sensitive compounds. The Fétizon oxidation is a good process for obtaining lactones from a diol because of its high reactivity with lactols. Polar groups in the reaction system, as well as steric hindrance of the alcohol's -hydrogen, greatly hinder the reaction. The oxidation of primary and secondary alcohols using silver (I) carbonate adsorbed into the surface of celite, commonly known as Fétizon's reagent, is known as Fétizon oxidation. Cabon monoxide is a hazardous byproduct of this process. These ketone bond forming reactions have several advantages. These ketone bond formation reactions have certain disadvantages, such as low atom efficiency and the production of a substantial amount of undesirable toxic byproducts [12].



Scheme 1.3: Jones oxidation for ketone-bond formation.

Dess–Martin periodinane

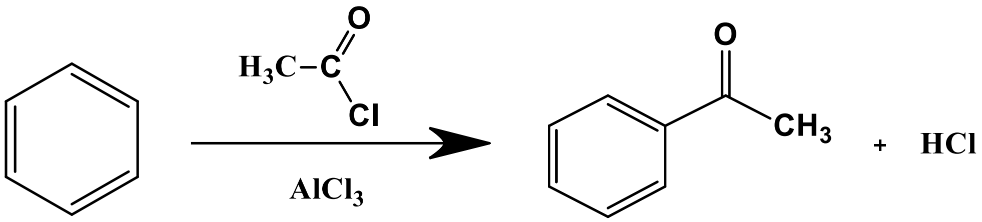
For the conversion of alcohols to aldehydes or ketones, the Dess–Martin periodinane is a moderate oxidant. The process is carried out under conventional circumstances, at room temperature, with dichloromethane as the most common solvent. After that, the product is separated from the spent periodinane Mixture of compound produce, as well as a considerable number of byproducts [13].



Scheme 1.4: Dess–Martin periodinane for ketone-bond formation

Friedel-Crafts acylation

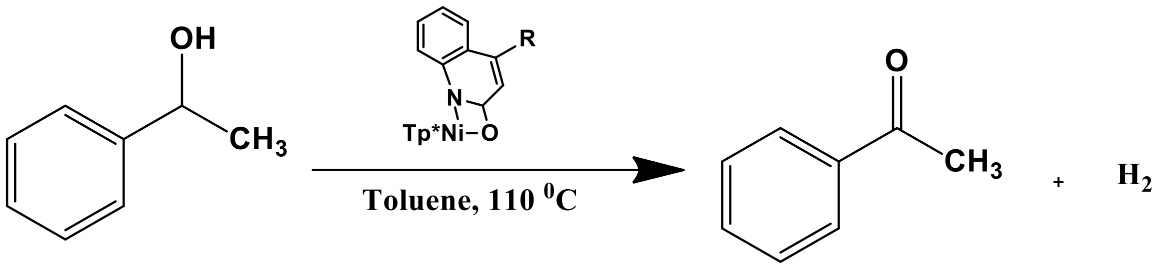
Aromatic ketones are made using Friedel Crafts acylation. A classic Friedel-Crafts acylation is the production of acetophenone from benzene and acetyl chloride. The poisonous byproduct of this reaction is HCl. These ketone bond formation reactions have certain disadvantages, such as low atom efficiency and the production of a substantial amount of undesirable toxic byproducts [14].



Scheme 1.5: Friedel-Crafts acylation for ketone-bond formation.

1.4.2. Homogeneous Catalytic Method

In this reaction 1- phenyl ethanol reacts with nickel complex in presence of toluene reflux condition at 110 °C to form Acetophenone and hydrogen gas. Homogeneous catalysts such as Ni-complex and Fe - complex were reported for the synthesis of ketones by dehydrogenation reactions. However, these homogeneous catalytic methods have some drawbacks including difficulties in catalyst/product separation and catalyst reuse. On the other hand, heterogeneous catalysts, such as hydrotalcite-supported gold Nano-particles, hydrotalcite-supported Cu Nano-particles, and chromium oxide-supported Cu Nano-particles were reported as a heterogeneous catalyst to synthesize ketones by dehydrogenation of secondary alcohols. However, these methods were encountered with high catalyst loading in presence of various acceptors, and in some cases, toxic chemicals were required. Though homogeneous catalysts are effective for ketone synthesis it has some drawbacks reusability of catalyst and separation of product from reaction mixtures [15-29].

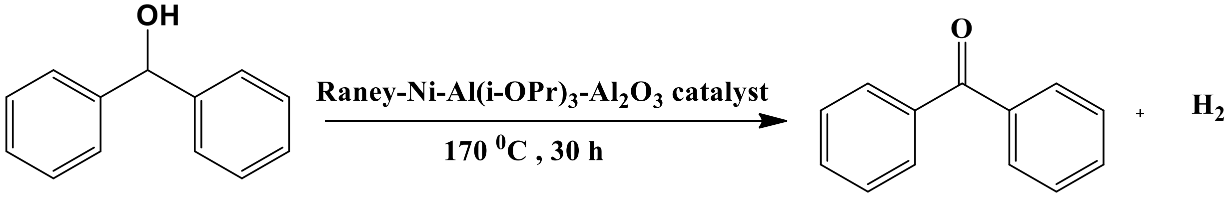


1-phenyl ethanol Acetophenone

Scheme 1.6: Homogeneous catalytic method for ketone-bond formation.

1.4.3. Previous Heterogeneous Catalytic Method

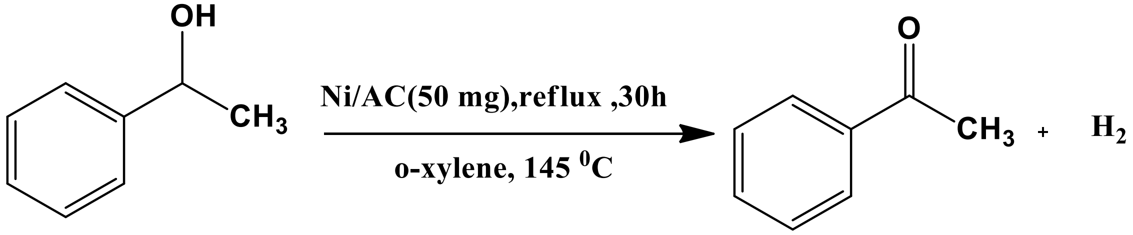
3 percent (weight mass) of freshly made Raney-Ni, 5 percent (w/w) of Al(i-OPr)3, and 5 percent (w/w) of Al_2O_3 were added to degassed alcohol (0.1 mol). This mixture was magnetically stirred and heated for 6 to 50 hours under nitrogen. The catalyst was removed by filtration under an inert atmosphere and washed with petroleum ether. The filtrate was then purified in vacuo by fractional distillation, giving 52-95 percent pure carbonyl compounds. The catalyst (a combination of Ni and alumina) that was removed by filtration was reused. Raney nickel catalyzed selective dehydrogenation of alcohol was reported but, in this method, they used aluminum isopropoxide as an additive. Though Heterogeneous catalysts were effective for ketone synthesis it has some drawbacks product/catalyst separation was difficult, low Percentage of yield, and additives were used in the reaction [30-43].



Scheme 1.6: Heterogeneous catalytic method for ketone-bond formation.

1.4.4. Heterogeneous Catalytic Method

5 percent (weight mass) of freshly manufactured Ni, Ni/Al_2O_3, Ni/TiO_2, Ni/CeO_2, and Ni/Nb_2O_5 supported catalyst was added to degassed alcohol (1mmol). This mixture was magnetically stirred and heated for 30 hours under a nitrogen atmosphere. The catalyst was separated from the reaction mixtures by filtration, which was then washed with acetone. The filtering was then purified using Column Chromatography. The selective dehydrogenation of alcohol catalyzed by Raney nickel has been described, however, the process employed aluminum isopropoxide as an adjuvant. The substrate scope of this approach was limited, and it could only be used for one reaction. It was planned to develop a more convenient and effective technique for synthesizing ketones from readily available secondary alcohol utilizing a heterogeneous catalyst to overcome the drawbacks above. As a result, the development of a heterogeneous catalytic system in which acceptors borrow hydrogen and were reused multiple times was more beneficial. We present a simple, mild, and efficient heterogeneous catalytic technique for the production of ketones by dehydrogenation of secondary alcohols utilizing an activated carbon-supported nickel Nano catalyst (Ni/AC) in this paper.



1-phenyl ethanol

Acetophenone

Scheme 1.7: Heterogeneous catalytic method for ketone-bond formation.

1.5. Concluding Remarks

Heterogeneous nickel Nano supported catalysts can be effective catalysts for the direct synthesis of ketone from secondary alcohol, avoiding the constraints of the previous technique in ketone synthesis. Heterogeneous catalysts are recyclable, easy to separate product from the catalyst, and have a high atom economy.

1.5.1. Why Do Choose Ni & AC for Ni/AC Catalyst?

Nickel (Ni) is more susceptible than other metals (Ag, Au, Pt, Co) because of its,

The AC (activated carbon) used as a support material is more efficient than other materials (Al_2O_3, TiO_2, CeO_2 & Nb_2O_5) because of its,

- Low cost
- High availability
- Less toxicity
- High mechanical resistance
- High surface area
- Good reductive properties

1.5.1. Table 01: Surface areas of different catalyst samples

Sample	Surface area (Sq.m/gm)
AC	1000
Nb_2O_5	54
CeO_2	81
Al_2O_3	161
TiO_2	47

Chapter 2

Experimental

2.1. Materials and Instruments

2.1.1. Chemicals and Reagents

The chemicals and reagents used in this research were analytical grade and commercial grade. Ethanol, ethyl acetate and 1-phenyl ethanol were purified by distillation. Other solvent such as acetone, n-hexane, chloroform, 2-propanol, o-xylene and chemicals were analytical grade used without further purification. The chemicals and reagents which were used in this research are given below:

- Ethanol
- Acetone
- n-hexane
- toluene
- chloroform
- 2-propanol
- o-xylene
- 1-phenyl ethanol
- Niobium pentaoxide
- Titanium oxide
- Aluminium oxide
- Cerium oxide
- Nickel Suphate
- Activated Carbon
- TLC plate

2.1.2. Instruments

To carry out the research processes and manufacture the ketone compounds, I employed a variety of equipment provided by the university. Many other tools were employed to examine the substances that had been created. I operated some of them myself, and I enlisted the assistance of an expert to operate others. The following instruments were used to conduct the research, analyze the produced amides, and characterize the catalyst:

- Round bottom flask
- Condenser set
- Heating bath
- Ice bath
- Magnetic stirrer hot plate
- Distillation unit
- Column chromatography
- Vacuum drier
- Furnace
- Fourier Transform Infrared Spectrophotometer (Shimadzu FT-IR-8400)
- Nuclear Magnetic Resonance Spectrometer (Bruker BPX- 400)
- Centrifuge Machine (Model-800, China)
- Digital Balance (Precision electrical balance)
- Rotatory Evaporator
- Oven
- UV-light

2.2. Method of Catalyst Synthesis Ni/AC (1:9)

In the first step, 0.025 mol nickel sulfate was taken in a beaker and dissolved in distilled water to prepare the nickel sulfate solution. After that, activated carbon was added to this solution, and the mixture was heated for 15 minutes at 80 degrees Celsius with continuous stirring. This mixture was evaporated with an evaporator and dried in a hot oven for 6 hours at 90 degrees Celsius. Then the solid mixture was calcined for 2 hours at 400 degrees Celsius. The reduction of the supported precursors was performed in a two necked reaction flask fitted with a reflux condenser under heated in sand bath at 100ºC under continuous stirring in presence of $N_2H_4.H_2O$ and NaOH solution to maintain the desired pH. After reduction, the mixture was filtrated off and washed with distilled water and 99 percent ethanol. To obtain the desired Ni/AC catalyst, the desired catalyst was dried in an oven at 110°C for 6 hours. Then it was characterized by several modern techniques such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) [44-46]. Then the catalytic activity of Ni/AC was checked and evaluated by a model reaction. In aqueous media, the above-mentioned precursor was reduced by the following reaction:

$$2Ni^{2+} + N_2H_4 + 4OH^{-} \longrightarrow 2Ni^{0} + N_2 + 4H_2O$$

Scheme 2.2.1: Catalytic reduction mechanism

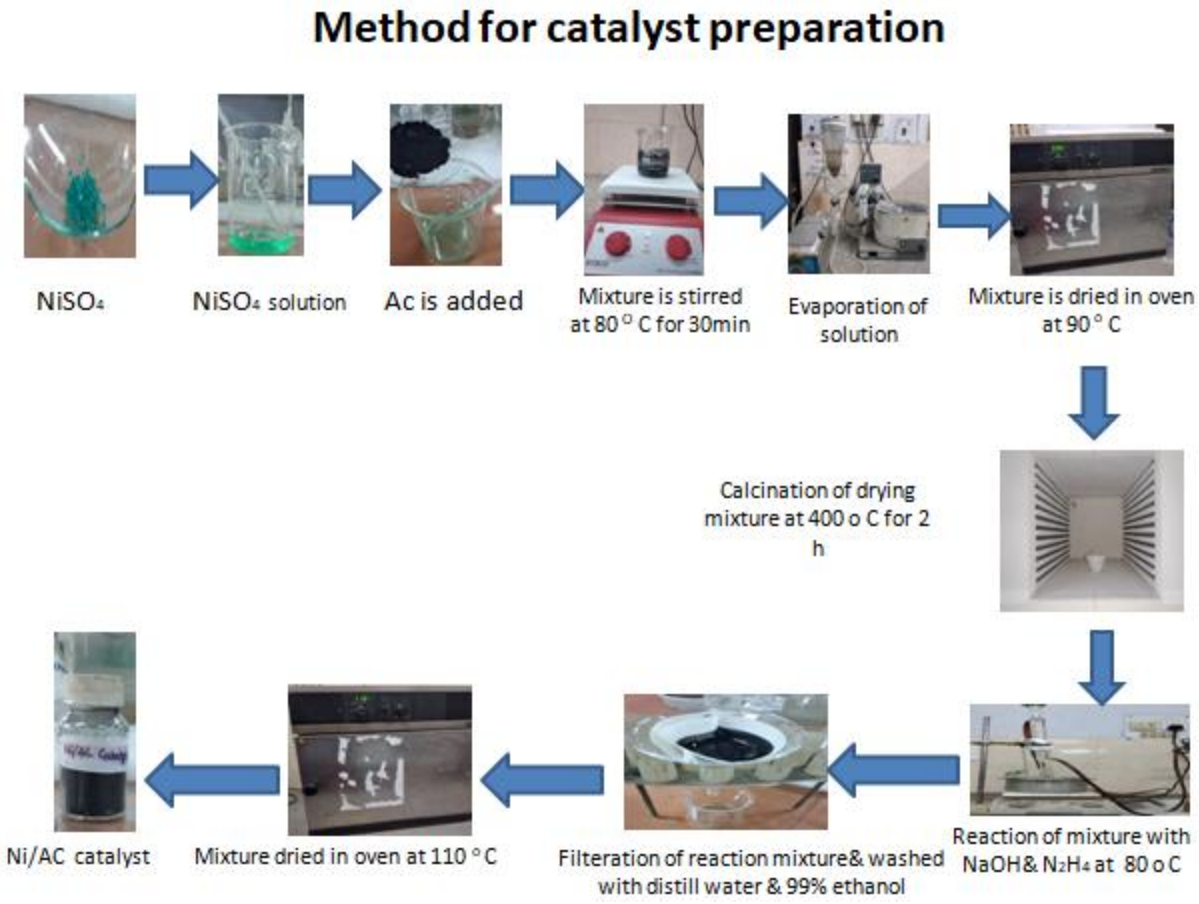


Figure 2.2.1: Method for Ni/AC catalyst preparation

2.2.2. Method of Catalyst Synthesis 1:9

Following the previous procedure to prepared

- Ni/Al_2O_3 Catalyst
- Ni/TiO_2 Catalyst
- Ni/CeO_2 Catalyst
- Ni/Nb_2O_5 Catalyst
- Ni catalyst

Figure .2.2.2 : Prepared catalyst

2.2.3. Another Method of Catalyst Synthesis Ni/TiO_2 (1:9)

liquid phase chemical reduction method Ni/TiO_2 (1:9)

Titanium dioxide powder was impregnated into 20 mL of $NiSO_4$ solution (0.25 mol L -1) with vigorous stirring at room temperature for 1 h. Then the resulting suspension was heated at 80 ℃ and stirred for 30 min. Then 35 ml solution of N_2H_4. H_2O and NaOH were added to the suspension with stirring for 15 min. Then the filtration of suspension and washed with distilled water with 99% ethanol. Then the mixture was dried in an oven at 110 °C for 6 h and to get the expected Ni/TiO_2 catalyst. Then it was characterized by several modern techniques such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) [47]. Then the catalytic activity of Ni/TiO_2 was checked and evaluated by a model reaction.

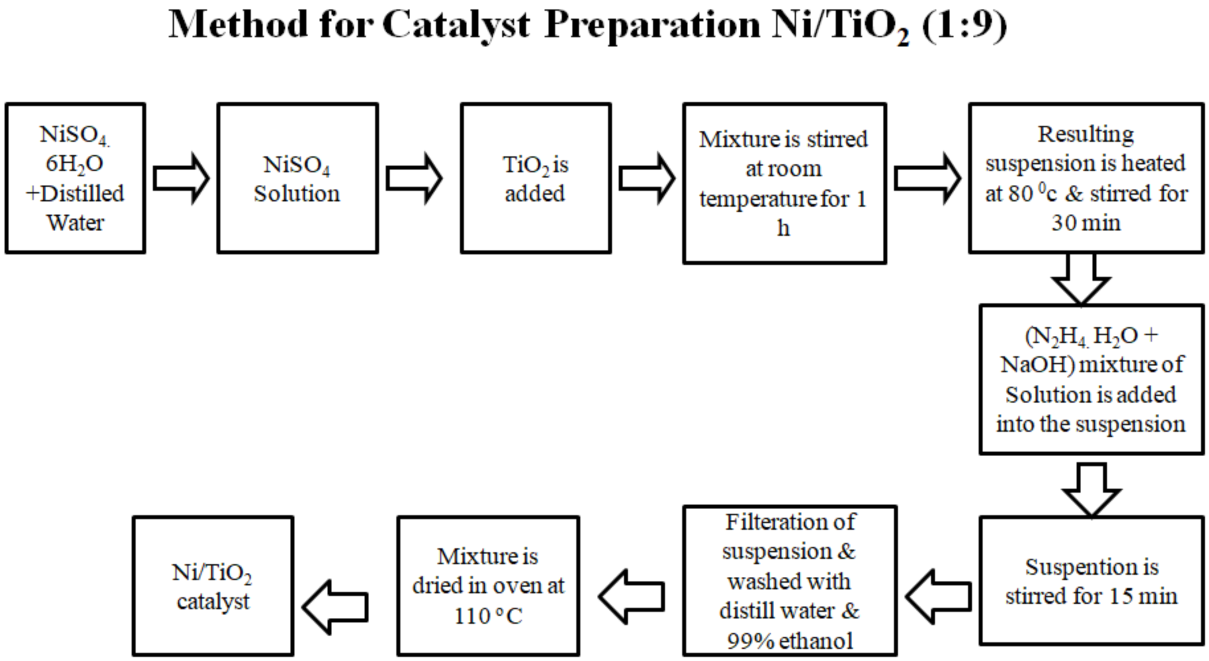


Figure .2.2.3: Liquid phase chemical reduction Method for Ni/TiO_2 catalyst preparation

2.2.5. Another Method of Catalyst synthesis (1:9)

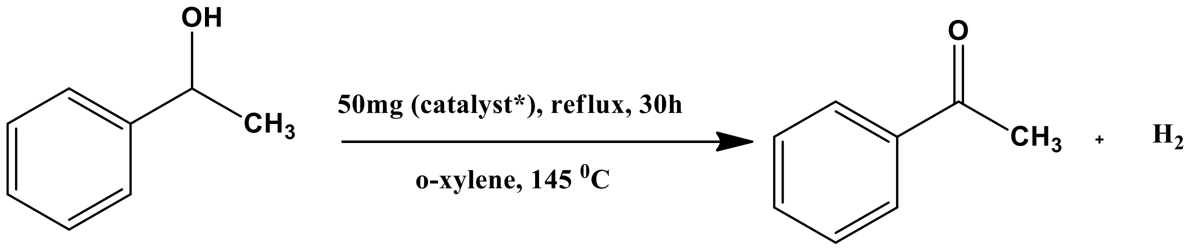
Following the previous procedure to prepared

- Ni/AC Catalyst
- Ni/Al_2O_3 Catalyst
- Ni/CeO_2 Catalyst
- Ni/Nb_2O_5 Catalyst
- Ni catalyst

Figure .2.2.4: Prepared catalyst

2.4.6. Ketone Synthesis

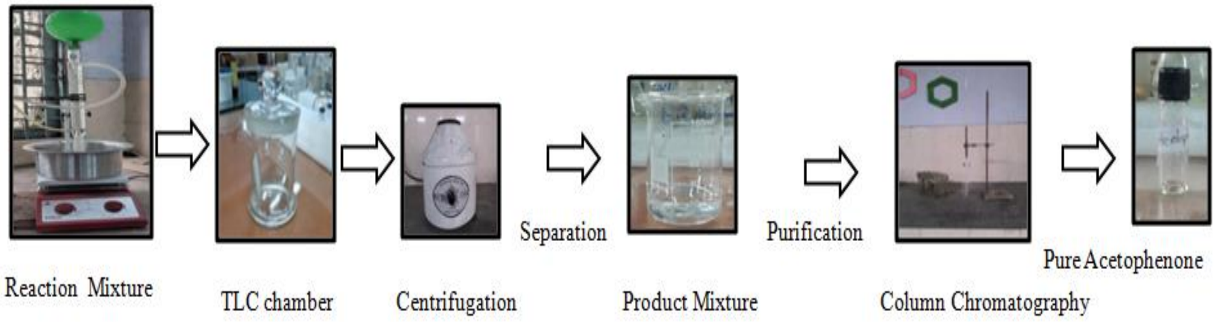
In this work, ketones were synthesized in a dehydrogenation reaction from secondary alcohols in presence of a heterogeneous catalyst. In a typical reaction vessel, 1 mmol secondary alcohol, 4 mL o-xylene, and 50 mg Ni nano-supported catalyst were introduced (RB flask). The reaction mixture was heated in a sand bath on a hot plate at 145 °C and stirred at 300 pm. After the reaction was completed, 2-propanol (4 mL) was added to the reaction mixture, and the Ni nano supported catalyst was separated from the reaction mixtures by centrifugation. Model reactions were used to check catalytic activity (Table 5). 1 mmol 1-phenyl ethanol, 4 mL o-xylene, and 50 mg Ni nano-supported catalyst were introduced to a reaction vessel for the model reaction (RB flask). Then the reaction mixture was heated in the presence of o-xylene under reflux conditions for 30 hrs. The progress of the reaction was monitored by thin layer chromatography (TLC) with n-hexane and chloroform appropriate solvent ratio. Then the completion of the reaction was confirmed by TLC and the solvent was removed from the reaction mixture by a rotatory evaporator. After completion of the reaction, the catalyst was separated from the reaction mixture by centrifugation, followed by washing with acetone, and dried at 100 °C for 3h. The reusability was checked for the recovered catalyst. Then the product was purified by column chromatography. Finally, the synthesized pure ketone product was characterized by using FT-IR, ^{1}H NMR, ^{13}C NMR, and GC-MS.



1-phenyl ethanol

Acetophenone

Scheme 2.2.1: Ketone synthesis



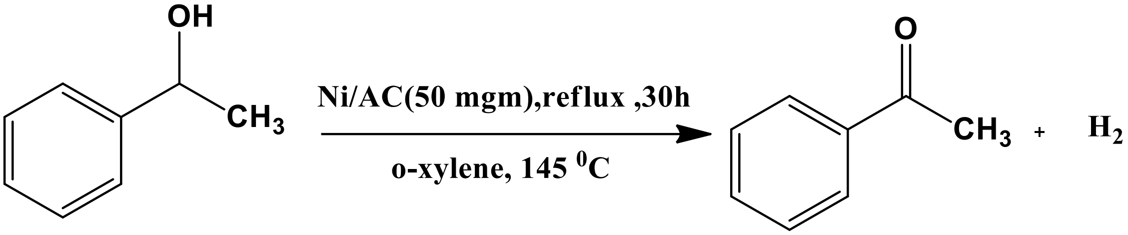
Separation and Purification

Figure .2.2.5: Separation & Purification for ketone Synthesis

2.4.7. Synthesis of Acetophenone

For the production of Acetophenone, 1 mmol of 1-phenyl ethanol was placed in an RB flask containing 50 mg Ni nano-supported catalyst and then added 4 mL of o-xylene to the mixture. This reaction mixture was heated on a hot plate at 145 °C in a sand bath for 30 hours with a continuous magnetic bar stirring at 300 pm. The progress of the reaction was monitored by thin layer chromatography (TLC) with n-hexane (1 ml) and chloroform (1 ml) appropriate solvent ratio. Then the completion of the reaction was confirmed by TLC. After completing the reaction 2 mL 2-propanol was added to the reaction mixtures and the Ni nano - supported catalyst was separated from the reaction mixtures by centrifugation. Then the catalyst was washed with acetone, and dried at 110 °C for 3 hours. The recovered Ni nano-supported catalyst was reused for three cycles without a significant reduction in product yield. A rotatory evaporator was used to extract the solvent from the reaction mixtures. Then the product was purified by column chromatography. Finally, the synthesized pure ketone product was characterized by using FT-IR,

^{1}H NMR,^{13}C NMR, and GC-MS. For catalyst screening, solvent screening, and temperature screening same reaction procedure was performed.



Scheme 2.2.2: Synthesis of 1-phenyl ethanol.

Molecular weight: Molecular weight: 120 g/mol

Molecular formula: C_8H_8O

Melting point: 20.2 ^{0}C

FT-IR (υ KBr): 1686, 1600,1450,1360,1267 cm-1

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.94-7.92 (m,1H), 7.44-7-4.41 (m,2H), 7.55-7.51 (m,2H), 2.57(s,3H)

^{13}C-NMR (100 MHz, $CDCl_3$): - δ 198.13 (C=O), 137.15, 128.58, 128.31, 133.10, 26.59

GC-MS ($CDCl_3$): m/e 120, 105, 77

2.3. Characterization of Synthesized Product

2.3.1. Fourier transform Infrared (FTIR) Analysis

The infrared spectra of the synthesized ketones were recorded on an FT-IR spectrometer in the region of 4000-500 cm-1. All the ketone samples had dried. A small portion of samples was taken and mixed with KBr [50, 51]. The powder mixtures were then compressed in a metal holder under pressure to make pellets. The pellets were then placed in the path of the IR beam for measurements.

2.3.2. Nuclear Magnetic Resonance (NMR) Analysis

^{1}H and ^{13}C-NMR spectra were recorded by Bruker BPX- 400 spectrometer operating at 400 MHz and 100 MHz respectively and $CDCl_3$ was used as a solvent, tetramethyl silane (TMS) as an internal standard. All chemical shifts (δ) were reported in ppm and coupling constants (J) in Hz. Chemical shifts were performed relative to tetramethyl silane (TMS) and d-solvent peaks (7.28 ppm in ^{1}H and 77.00 ppm in ^{13}C, chloroform), respectively. Abbreviations used in the NMR experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet [50-51].

2.3.3. Gas Chromatography Mass Spectrum (GC-MS) Analysis

Retention time and mass spectrum for acetophenone were recorded using columns: Rxi-5ms, 30m, 0.25mm ID, and 0.25µ df by Shimadzu GC-MS. To determine the mass spectrum the molecule is bombarded with a high electron beam and then forms a molecular ion again fragmentation of molecular ion occurs from many fragment ions [50-51].

2.3.4. X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns were performed for calcinated Ni/AC catalyst at 400 °C before being used in the reaction and after three cycles in the powder state. The powder samples were pressed in a square aluminum sample holder (40 mm × 40 mm) with a 1 mm deep rectangular hole (20 mm x 15 mm) and pressed against an optical smooth glass plate. The upper surface of the sample was labeled in the plane with its sample holder. The sample holder was then placed in the diffractometer.

2.3.5. Melting Point

Melting points of ketones were determined in open capillary tubes in the melting point apparatus.

2.3.6. Solubility

All the ketones were soluble in chloroform

Chapter 3

Results and Discussions

3.1. Characterization of Synthesized Ni/AC Catalyst:

3.1.1. Magnetic Behavior of Ni/AC Catalyst:

The magnetic behavior of the synthesized activated carbon-assisted nickel nano catalyst was demonstrated. Nickel nanoparticles with an activated carbon-supported nickel nano catalyst display magnetic characteristics.

Fig .3.1.1: Magnetic Behavior of Ni /AC catalyst

3.1.2: Analysis of SEM for Synthesized Ni/AC

The chemical structures (Ni loadings) of the samples were determined using scanning electron microscopy and X-ray diffraction, and the prepared catalysts and commercial catalysts were compared. This study used scanning electron microscopy to examine the results, and the image of (SEM) revealed that the activated carbon-supported nickel nano catalyst produced similar spectra to the commercial catalyst fig: (a) [48]. To determine the average particle size of a nickel nano is 35 nm, using an SEM picture. Because the precursors are protected from aggregation during crystallization, this was expected.

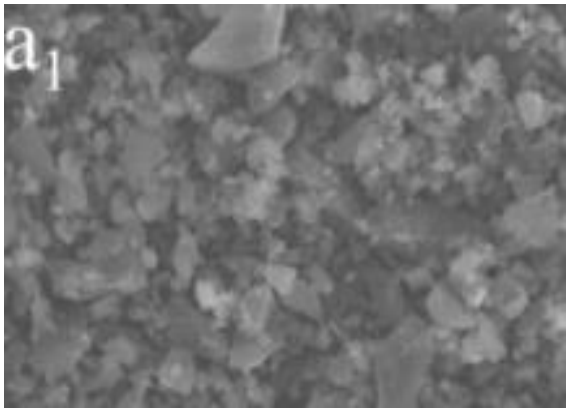
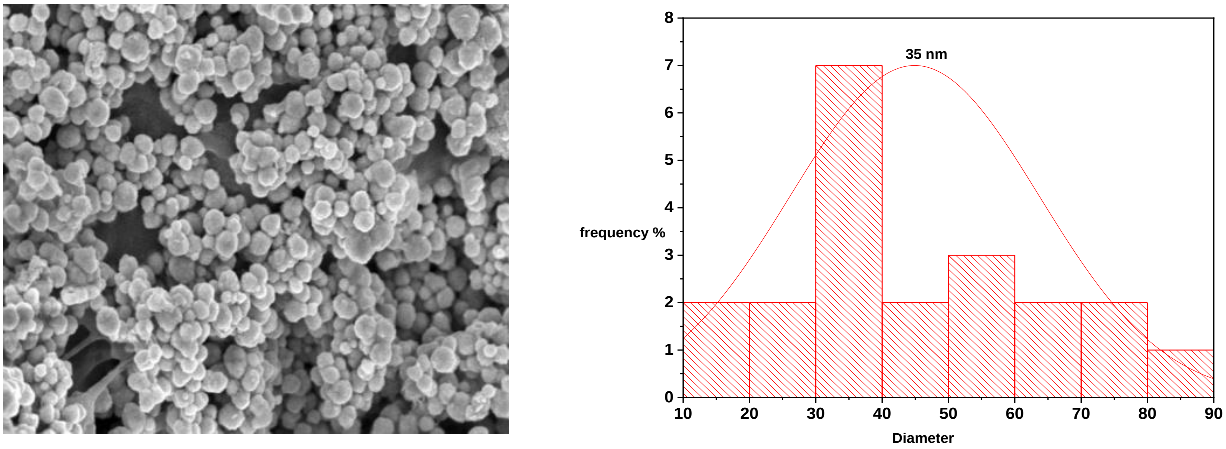


Figure. 3.1.2. (a): Literature SEM image



(b) (c)

Figure .3.1.3: (b) SEM image of crystalline structure Ni/AC (c) Determination of particle size

3.1.3. Analysis of Energy dispersive X-ray Spectroscopy (EDS) of Synthesized Ni/AC

EDS is a technique for determining which chemical elements are present in a sample and estimating their relative abundance. EDS can also be used to measure multi-layer metallic coatings and do alloy analysis. Several factors influence the accuracy of this quantitative sample composition analysis. The X-ray emission peaks of many elements will overlap. The type of sample has an impact on the accuracy of the measured composition. Any atom in the sample that is sufficiently stimulated by the incoming beam generates X-rays. Because these X-rays are emitted isotopically in all directions, they may not all leave the sample. The energy of an X-ray and the composition, amount, and density of the material it must pass through to reach the detector determine the possibility of an X-ray escaping the object and therefore being available to detect and quantify. Because of these and other X-ray absorption effects, reliable sample composition determination from the recorded X-ray emission spectrum necessitates the employment of quantitative correction techniques. Table 02: EDS measured the chemical composition of activated carbon-supported nickel nano catalyst.

3.1.4. Results and Discussions Table- 02: Chemical Composition of Ni/AC by determined EDS

Element	Atom %
C	86.64
Ni	13.36

3.1.5. Analysis of Energy- dispersive X-ray Spectroscopy (EDS) of Synthesized Ni/AC

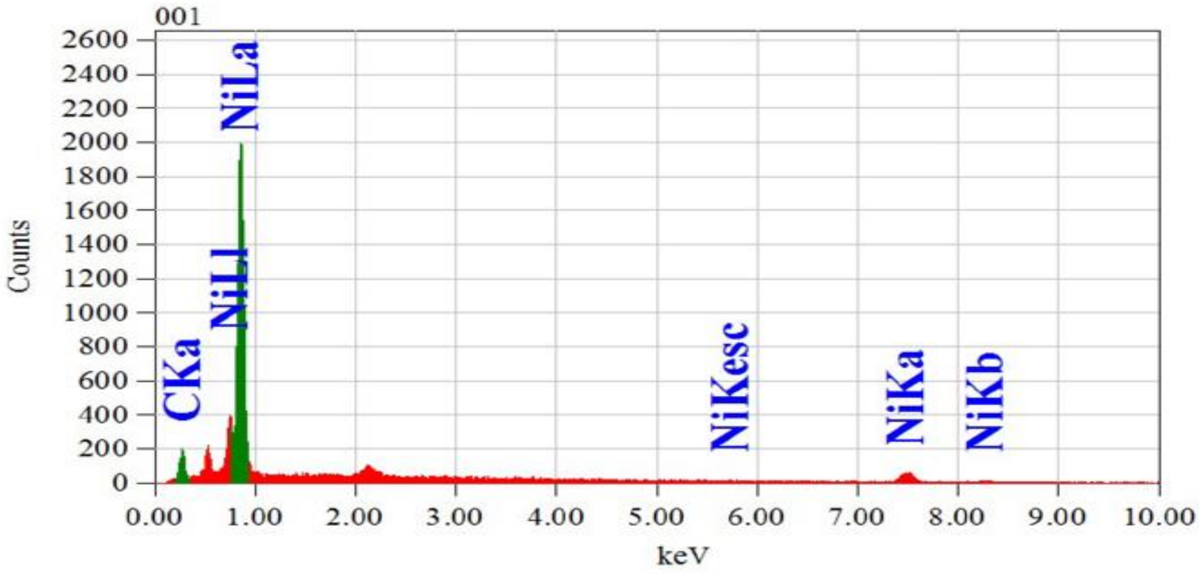
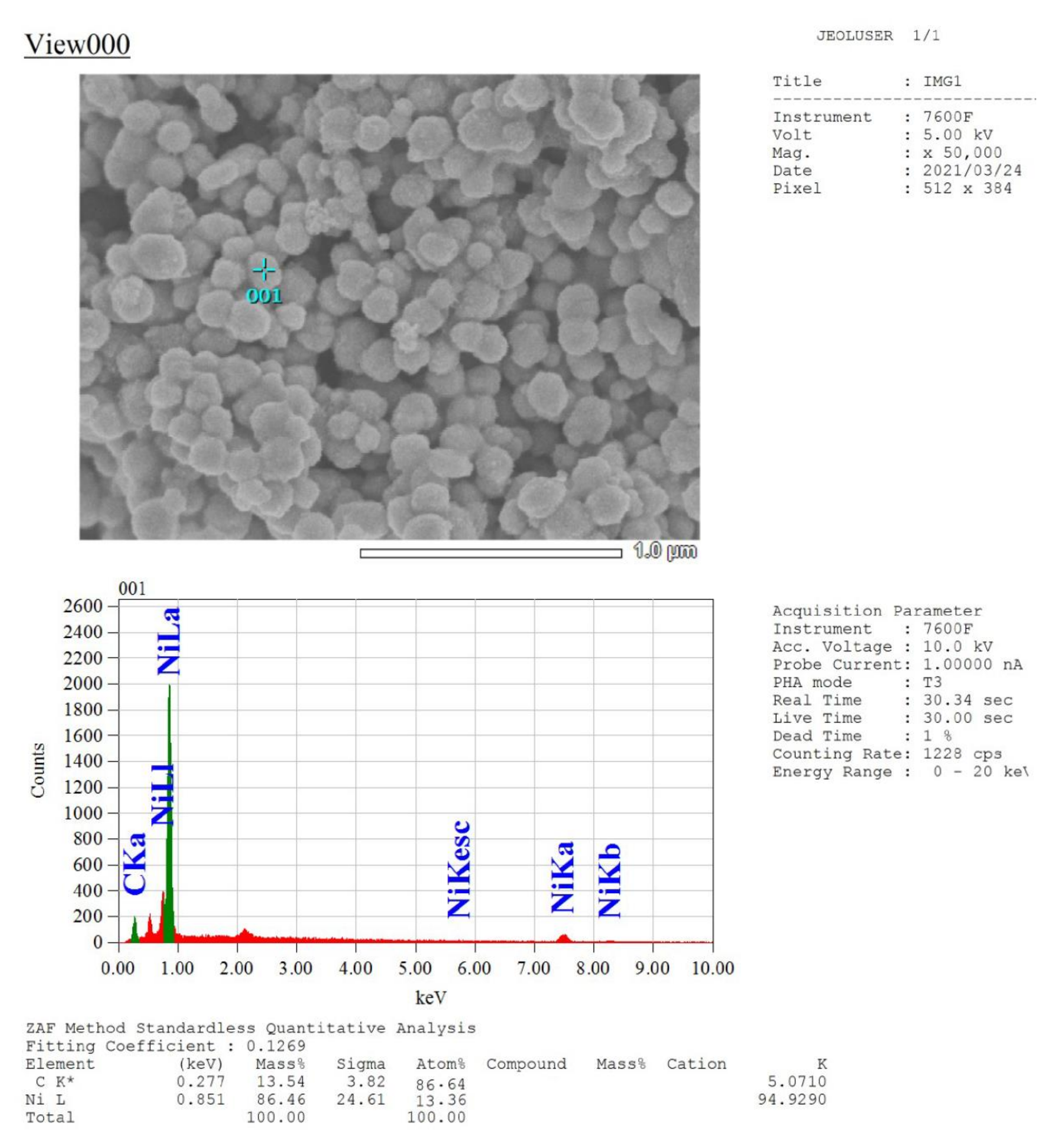


Figure .3.1.4: Chemical composition are based on EDS method



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PHA mode      : T3
Real Time     : 30.34 sec
Live Time     : 30.00 sec
Dead Time     : 1 %
Counting Rate: 1228 cps
Energy Range :   0 - 20 ke\
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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1269
Element         (keV)   Mass%   Sigma   Atom%  Compound     Mass%  Cation          K
 C K*           0.277   13.54    3.82   86.64                                 5.0710
Ni L            0.851   86.46   24.61   13.36                                94.9290
Total                  100.00          100.00
```

Figure .3.1.5: Energy- dispersive X-ray spectroscopy (EDS) of synthesized Ni/AC

3.1.6. Analysis of XRD for Synthesized Ni/AC

Crystalline Size of Ni/AC Catalyst by XRD Analysis:

Two synthetic approaches for Ni/AC nano catalyst production are discussed in this paper. The XRD patterns of the products from both methods were compared to the patterns of standard catalysts. Based on these findings, the two-step process for the synthesis of Ni nano catalysts from activated carbon was shown to be the most suited for producing Ni/AC nano catalyst in the pure phase. The pattern of impregnation generated Ni/AC nano catalyst of the sample calcined at 400 °C for 2 h and the commercial catalyst was shown in the XRD figure (a) & (b) below. Which of the two is comparable to the XRD data [48].

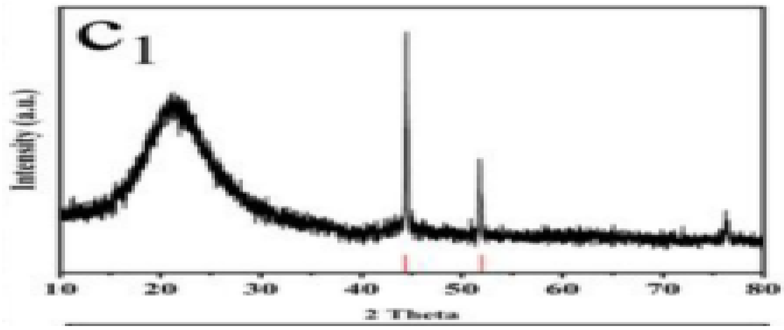


Figure .3.1.6. (a): Literature XRD

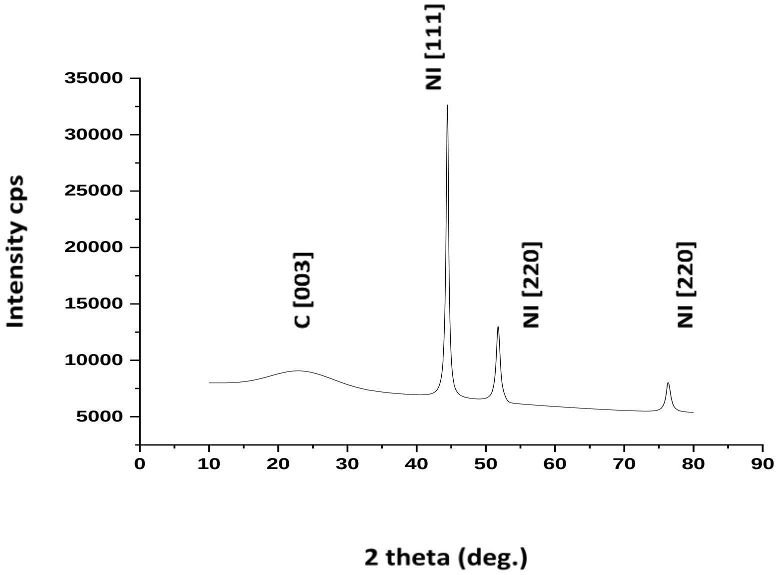


Figure .3.1.7 (b): Intensity (cps) vs 2 theta (deg.)

3.2. Analysis of SEM for Synthesized Ni/Al_2O_3

The chemical structures (Ni loadings) of the samples were determined using scanning electron microscopy and X-ray diffraction, and the prepared catalysts and commercial catalysts were compared. In this work, scanning electron microscopy (SEM) analysis was performed, and the image of (SEM) revealed that manufacturing Aluminum supported nickel nano catalyst gave similar spectra to the commercial catalyst fig: (a) [46]. The average particle size of nickel nano is 59 nm, as determined from the SEM picture. Because the precursors are protected from aggregation during crystallization, this was expected.

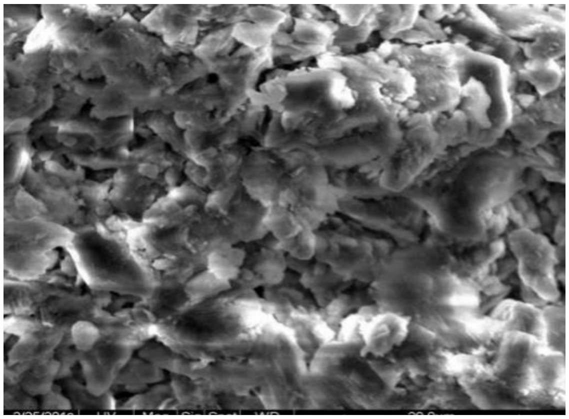
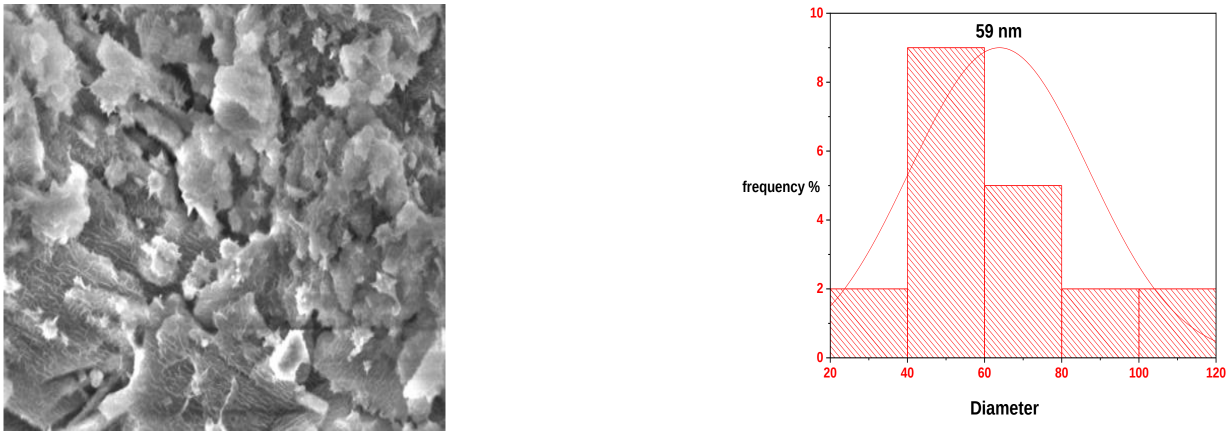


Figure.3.2.1. (a): Literature SEM image



(b) (c)

Figure .3.2.2: (b) SEM image of crystalline structure Ni/Al_2O_3 (c) Determination of particle size

3.2.1. Analysis of Energy dispersive X-ray spectroscopy (EDS) of Synthesized Ni/Al_2O_3

EDS is a technique for determining which chemical elements are present in a sample and estimating their relative abundance. EDS can also be used to measure multi-layer metallic coatings and do alloy analysis. Several factors influence the accuracy of this quantitative sample composition analysis. The X-ray emission peaks of many elements will overlap. The type of sample has an impact on the accuracy of the measured composition. Any atom in the sample that is sufficiently stimulated by the incoming beam generates X-rays. Because these X-rays are emitted isotopically in all directions, they may not all leave the sample. The energy of an X-ray and the composition, amount, and density of the material it must pass through to reach the detector determine the possibility of an X-ray escaping the object and therefore being available to detect and quantify. Because of these and other X-ray absorption effects, reliable sample composition determination from the recorded X-ray emission spectrum necessitates the employment of quantitative correction techniques. Table 03: EDS determined chemical composition of aluminum supported nickel nano catalyst.

3.2.2. Results and Discussions Table-03: Chemical Composition of Ni/Al_2O_3 by determined EDS

Element	Atom %
O	**64.88**
Al	**24.62**
Ni	**10.50**

3.2.3. Analysis of Energy- dispersive X-ray Spectroscopy (EDS) of Synthesized Ni/Al_2O_3

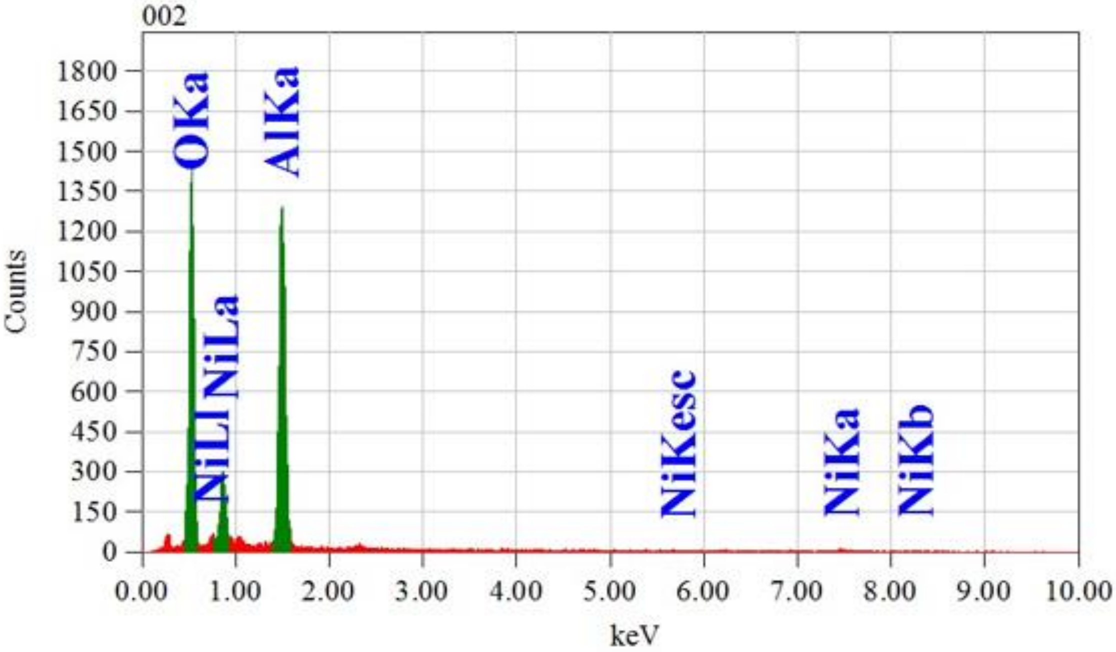
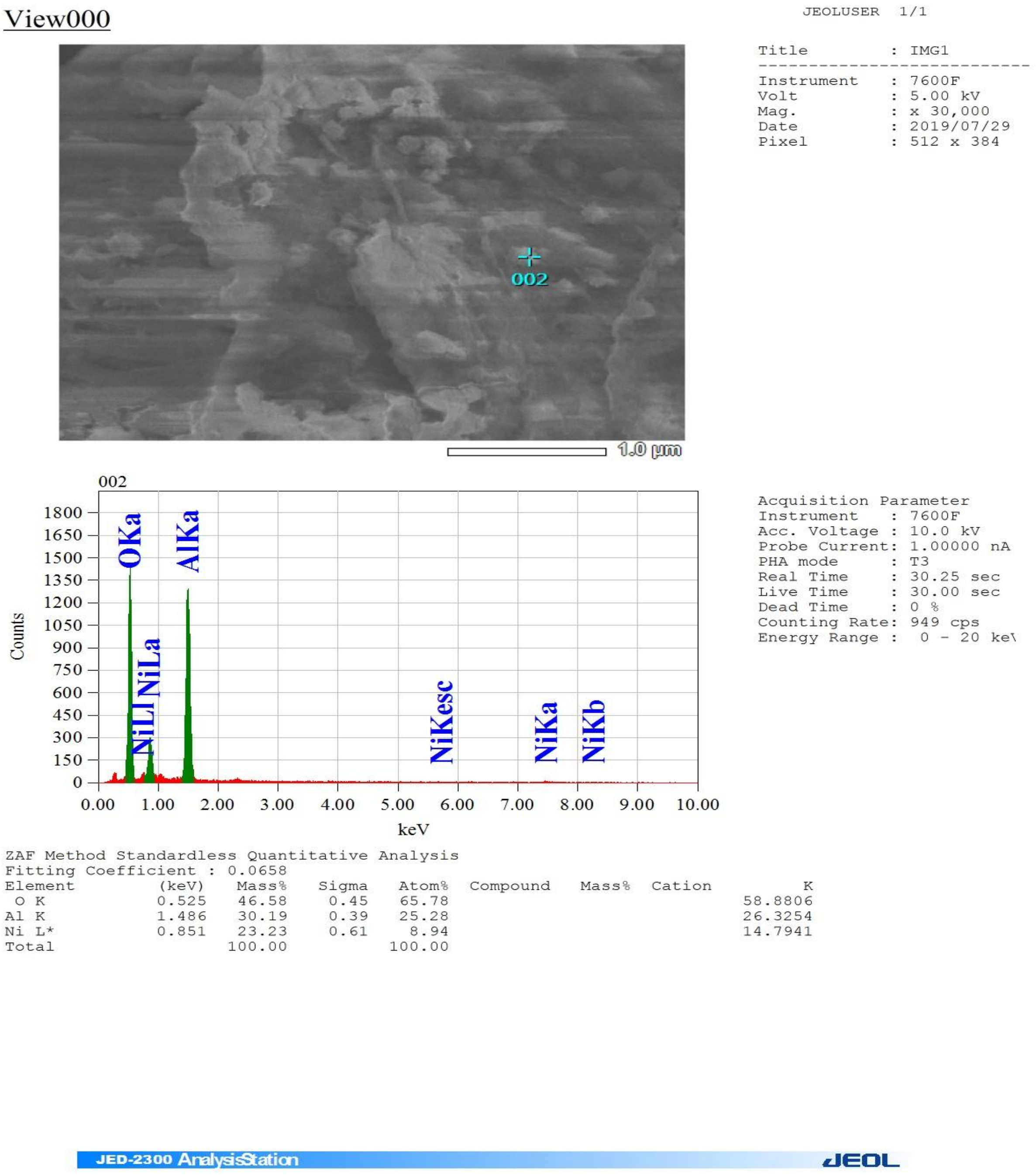


Figure.3.2.3: Chemical composition are based on EDS method



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PHA mode      : T3
Real Time     : 30.25 sec
Live Time     : 30.00 sec
Dead Time     : 0 %
Counting Rate: 949 cps
Energy Range :   0 - 20 keV

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.0658
Element         (keV)    Mass%    Sigma    Atom%  Compound    Mass%  Cation          K
 O K            0.525    46.58     0.45    65.78                                58.8806
Al K            1.486    30.19     0.39    25.28                                26.3254
Ni L*           0.851    23.23     0.61     8.94                                14.7941
Total                   100.00            100.00
```

Figure .3.2.4: Energy- dispersive X-ray spectroscopy (EDS) of synthesized Ni/Al_2O_3

3.3. Analysis of SEM for Synthesized Ni

The chemical structures (Ni loadings) of the samples were determined using scanning electron microscopy and X-ray diffraction, and the prepared catalysts and commercial catalysts were compared. In this work, scanning electron microscopy (SEM) analysis was performed, and the image (SEM) revealed that the prepared nickel catalyst had similar spectra to the commercial catalyst fig: (a) [49]. To determine the average particle size of a nickel nano is 46 nm, using an SEM image.

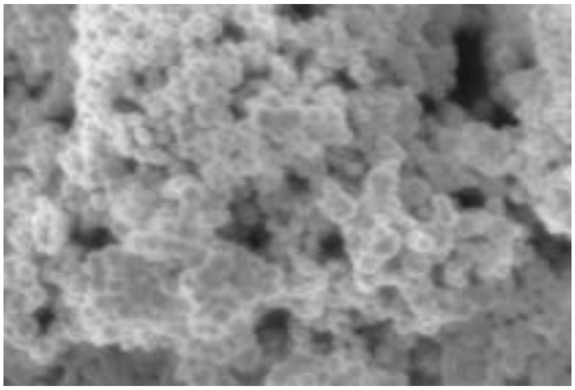
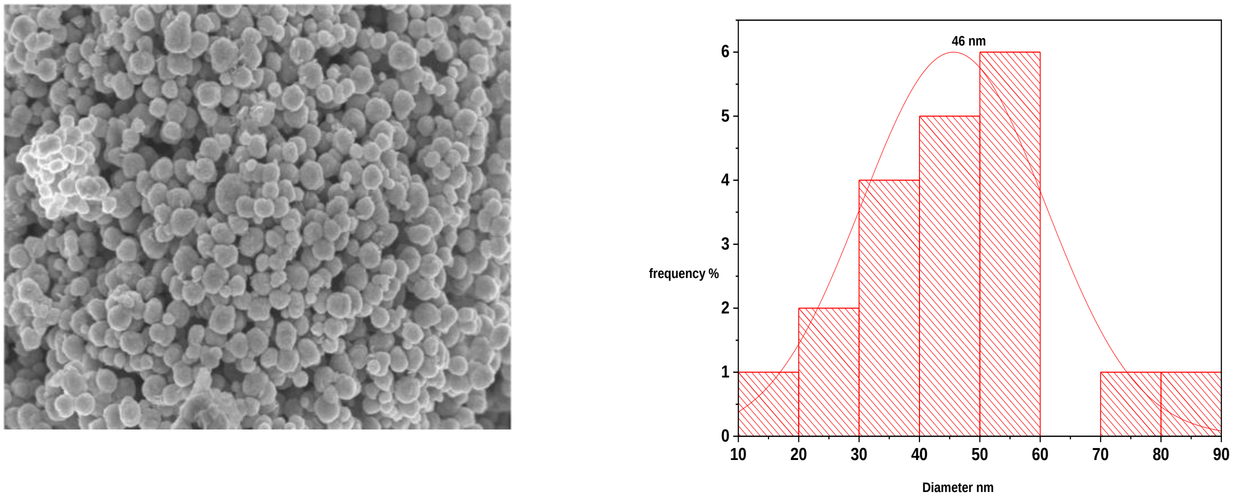


Figure. 3.3.1.(a): Literature SEM image



(b)

(C)

Figure.3.3.2: (b) SEM image of crystalline structure Ni (c) Determination of particle size

3.3.1. Analysis of Energy dispersive X-ray Spectroscopy (EDS) of Synthesized Ni

EDS is a technique for determining which chemical elements are present in a sample and estimating their relative abundance. EDS can also be used to measure multi-layer metallic coatings and do alloy analysis. Several factors influence the accuracy of this quantitative sample composition analysis. The X-ray emission peaks of many elements will overlap. The type of sample has an impact on the accuracy of the measured composition. Any atom in the sample that is sufficiently stimulated by the incoming beam generates X-rays. Because these X-rays are emitted isotopically in all directions, they may not all leave the sample. The energy of an X-ray and the composition, amount, and density of the material it must pass through to reach the detector determine the possibility of an X-ray escaping the object and therefore being available to detect and quantify. Because of these and other X-ray absorption effects, reliable sample composition determination from the recorded X-ray emission spectrum necessitates the employment of quantitative correction techniques. Table 04: Nickel catalyst chemical composition as measured by EDS.

3.3.2. Results and Discussions Table -04: Chemical Composition of Ni by determined EDS

Element	Mass %	Atom %
Ni	100.00	100.00

3.3.3. Analysis of Energy- dispersive X-ray Spectroscopy (EDS) of Synthesized Ni

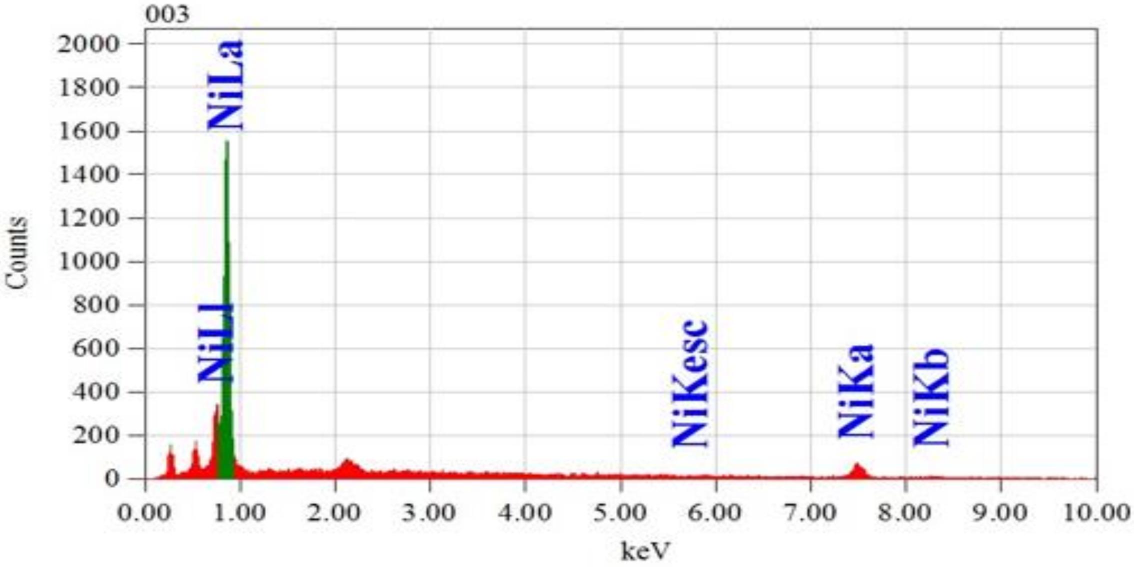
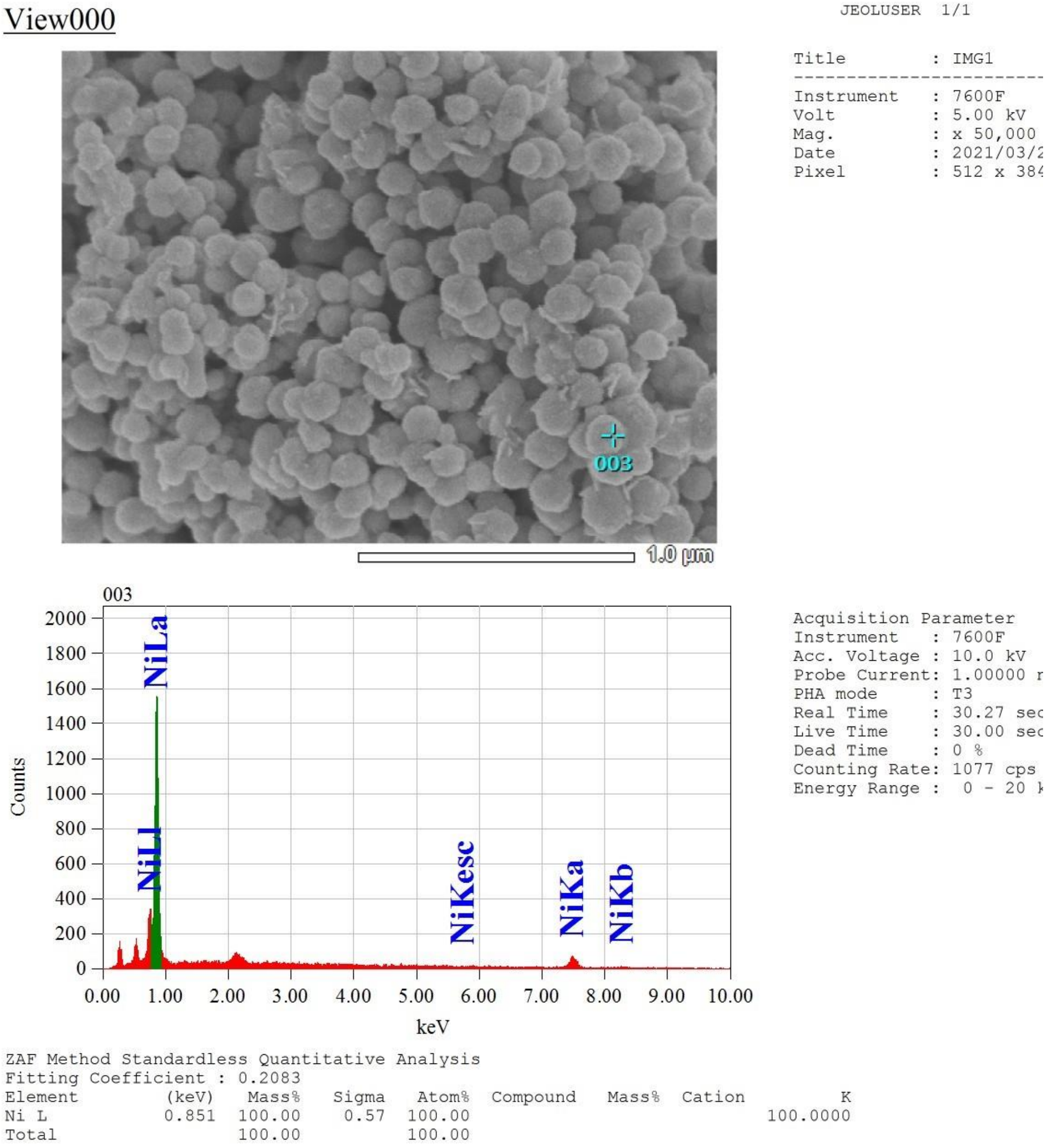


Figure. 3.3.3: Chemical composition are based on EDS method



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Live Time     : 30.00 sec
Dead Time     : 0 %
Counting Rate: 1077 cps
Energy Range :  0 - 20 k
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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2083
Element         (keV)   Mass%   Sigma   Atom%  Compound    Mass%  Cation          K
Ni L            0.851  100.00    0.57  100.00                                100.0000
Total                  100.00          100.00
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Figure .3.3.4: Energy- dispersive X-ray spectroscopy (EDS) of synthesized Ni

3.4. Catalyst Screening

The catalytic activity of the model reaction was tested. For this, I created a reaction condition in which no catalyst was utilized but all other parameters stayed the same. Under these conditions, the reaction produces no products. As a result, the reaction was clearly catalytic. Catalysts were tested for 30 hours at 145°C under reflux circumstances for the reaction of 1-phenyl ethanol. The yield of the corresponding ketone for various heterogeneous catalysts is summarized in Table-05, (Fig. 3.4.). We tested six different metal oxides. Activated carbon has the highest catalytic activity among these catalysts, with an 88 percent yield. The reaction produces H_2 gas, which leaves the process instantly. That's why it doesn't have the opposite effect.

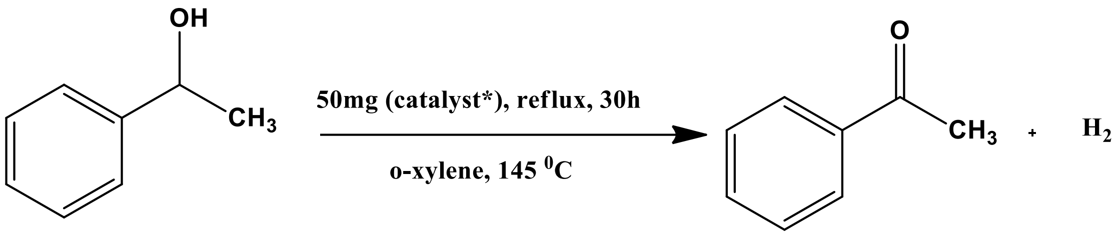
3.4.1. Solvent Screening

For the reaction of 1-phenyl ethanol, three types of solvent were utilized in solvent screening. The solvent o-xylene was found to be suitable for ketone production. We also see that there is no reaction without the presence of a solvent. The outcome of solvent screening is shown in Table-06, (Fig. 3.4.1.).

3.4.2. Reusability of Ni/AC

We tested the reusability of the Ni/AC catalyst for the reaction of 1-phenyl ethanol after the reaction was completed. The catalyst was removed from the reaction mixtures by centrifugation, washed with acetone, and dried at 110 °C for 3 hours. The recovered Ni/AC catalyst was reused for three cycles without significant loss of catalytic activity, but the result of this reaction decreased dramatically after the three cycles. Table No. 07 (Fig. 3.4.2.).

3.4 Catalyst screening for model reaction Model reaction



1-phenyl ethanol

Acetophenone

3.4. Table-05: Catalyst screening for model reaction

Entry	Ratio (Ni: Support)	Catalyst *	(%) Yield
01	-	no catalyst	0
02	1:9	Ni/AC	88
03	1:9	Ni/Nb_2O_5	80
04	1:9	Ni/CeO_2	60
05	1:9	Ni/Al_2O_3	50
06	1:9	Ni/TiO_2	40
07	-	Ni	20

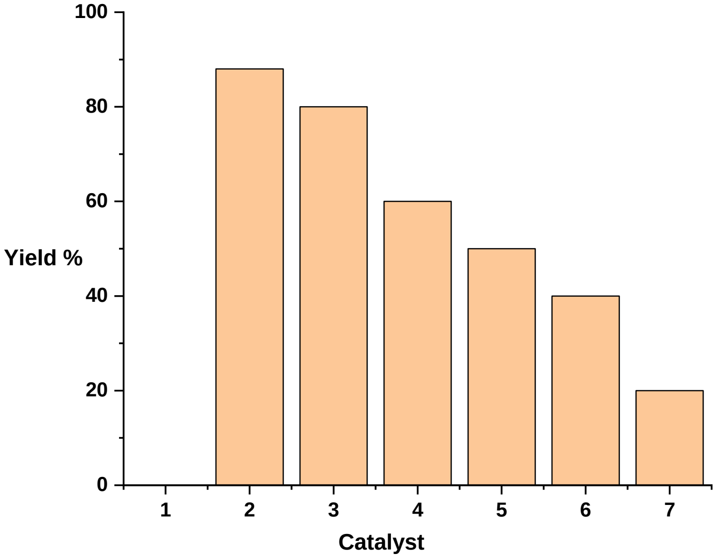
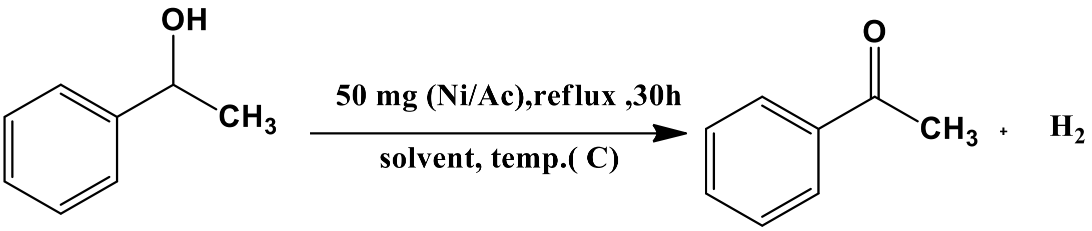


Fig.3.4.1: Catalyst screening for model reaction.

3.4.1 Solvent Screening for Model Reaction



1-phenyl ethanol **Acetophenone**

3.4.1. Table-06: Solvent screening for model reaction

Entry	Solvent	Temperature (^{0}c)	(%) Yield
01	O-xylene	reflux	88
02	Toluene	reflux	0
03	n-hexane	reflux	0
04	Without solvent	145^{0}c	0

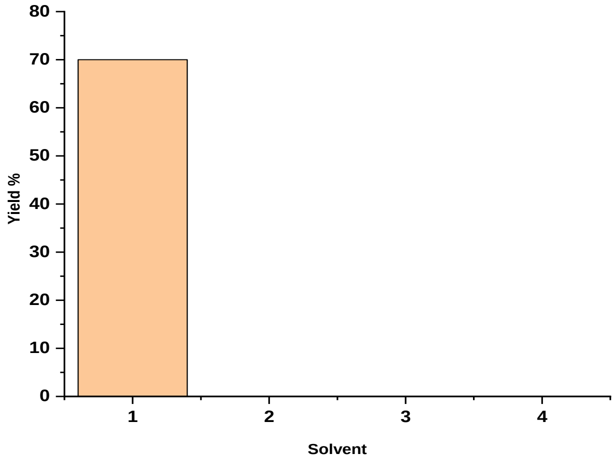
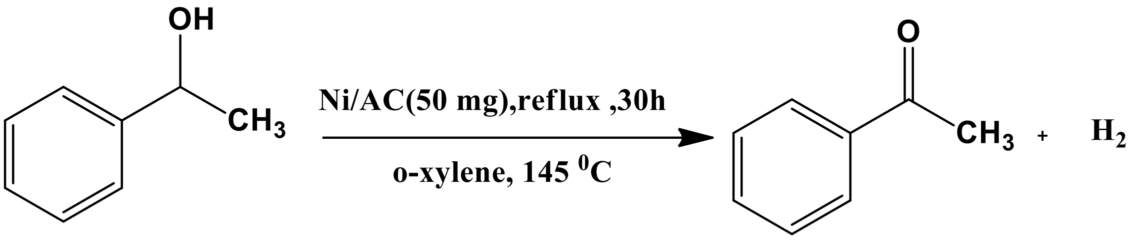


Fig.3.4.2: Catalyst screening for model reaction.

3.4.2. Reusability of Ni/AC for Model Reaction



1-phenyl ethanol

Acetophenone

3.4.2. Table- 07: Reusability of Ni/AC for Model Reaction

Cycle number	Yield (%)
1	88
2	78
3	68

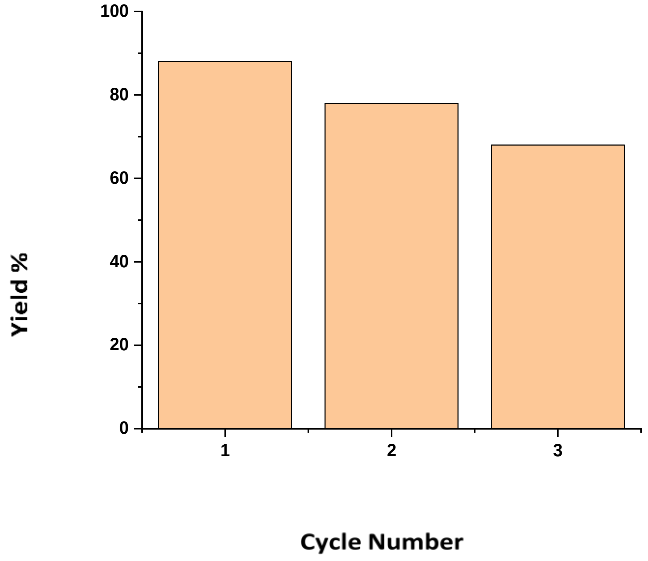


Fig.3.4.3: Reusability of Ni/AC for dehydrogenation of 1-phenyl ethanol in o-xylene reflux for 30 h

3.4.3. Recycle and Reusability

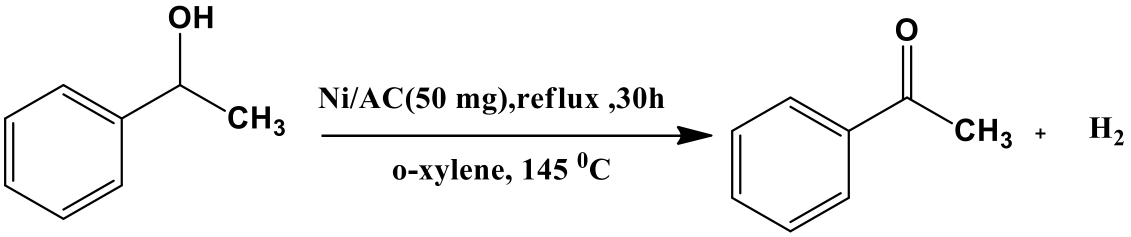
❖ Magnetic Behavior of the Reused Ni/AC Catalyst:

Fig.3.4.4: Magnetic behavior of the reused Ni/AC Catalyst

3.5. Characterization of Synthesized ketone

3.5.1. Characterization of Synthesized Acetophenone

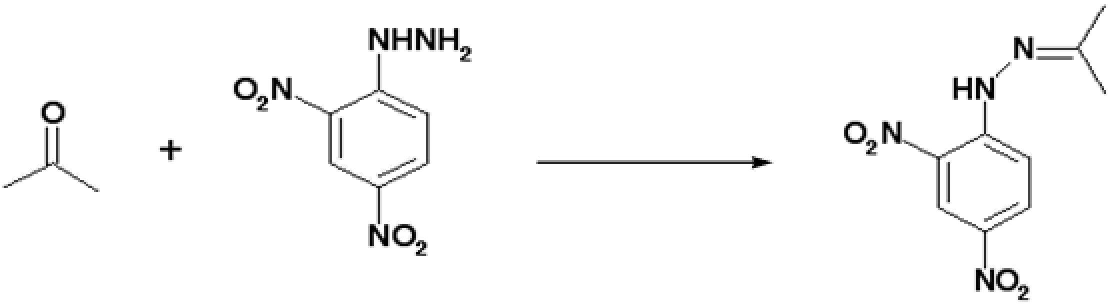
For the production of Acetophenone, 1 mmol of 1-phenyl ethanol was placed in an RB flask containing 50 mg Ni nano-supported catalyst and then added 4 mL of o-xylene to the mixture. This reaction mixture was heated on a hot plate at 145 °C in a sand bath for 30 hours with a continuous magnetic bar stirring at 300 pm. The progress of the reaction was monitored by thin layer chromatography (TLC) with n-hexane (1 ml) and chloroform (1 ml) appropriate solvent ratio. Then the completion of the reaction was confirmed by TLC. After completing the reaction 2 mL 2-propanol was added to the reaction mixtures and the Ni nano-supported catalyst was separated from the reaction mixtures by centrifugation. Then the catalyst was washed with acetone, and dried at 110 °C for 3 hours. The recovered Ni nano-supported catalyst was reused for three cycles without a significant reduction in product yield. A rotatory evaporator was used to extract the solvent from the reaction mixtures. Then the product was purified by column chromatography. Finally, the synthesized pure ketone product was characterized by using FT-IR, ^{1}H NMR,^{13}C NMR, and GC-MS.



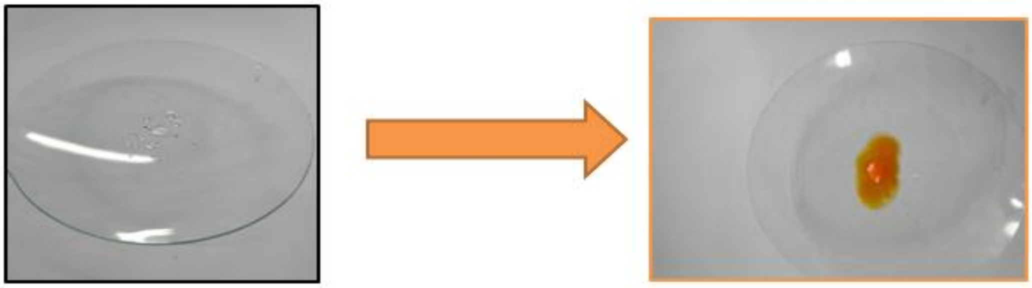
Scheme 3.5.1: Synthesis of acetophenone

3.5.2. Chemically Detection of Ketone Group

Dinitrophenylhydrazone orange precipitate was formed when ketone reacted with 2,4-Dinitrophenyl hydrazine. The sample compound was first placed in a wash glass. Then, to make Dinitrophenylhydrazone Orange Precipitate, when 2,4-DInitrophenyl hydrazine was added to the sample compound. This experiment revealed the presence of a carbonyl group in the sample compound [52].



Scheme 3.5.2: Chemically Detection of Ketone Group



Acetophenone

Dinitrophenylhydrazone Orange Precipitate

Fig.3.5.1: Chemically Detection of Ketone Group

3.5.3. Characterization of Synthesized Acetophenone by chemical spectroscopic method

i) FT-IR spectroscopy:

The FT-IR (KBr) spectrum (Figure.3.5.3, Page no. 70) of the ketone-1 exhibited a number of bands, some of which were assigned as the follows at v cm-1:

3.5.3. Table - 08: IR band of Acetophenone

Bonds	Wavelength (cm-1)
C=O (str.)	**1686**
C=C (str.)	**1600**
C=C (str.)	**1450**
O-C-C (bend)	**1267**
-CH_3 bend. (-C-H)	**1360**

ii) ^{1}H-NMR spectroscopy:

The 1H-NMR spectrums (Figure.3.5.4, Page no. 71) of ketone-1 exhibited signals (in δ ppm) which were assigned as follows:

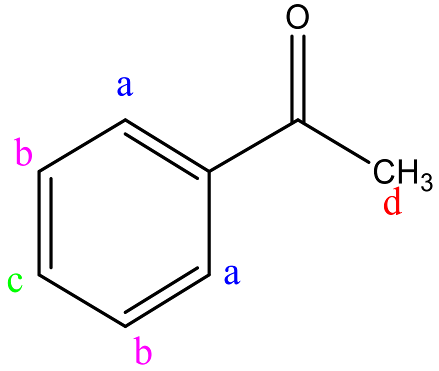
^{1}H NMR (400 MHz, $CDCl_3$, TMS):

a – δ 7.94-7.92 (m,2H)

b – δ 7.44- 7.41 (m,2H)

c – δ 7.55-7.51 (m,1H)

d – δ 2.57 (s,3H)



iii) ^{13}C-NMR spectroscopy:

The 13C-NMR spectrum (Figure.3.5.7, Page no. 74) of ketone-1 showed several signals (in δ ppm) which were assigned as follows:

^{13}C NMR (100 MHz, $CDCl_3$, TMS):

e - δ 198.13 (C=O)

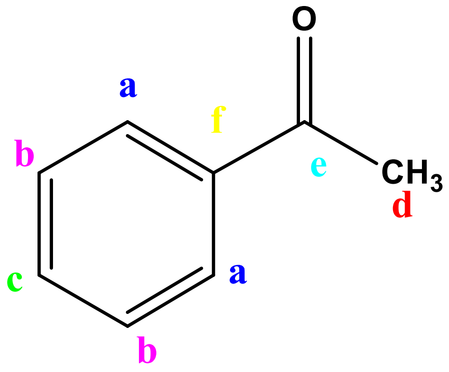
f – δ 137.15

b– δ 128.58

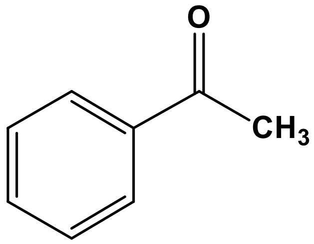
a– δ 128.31

c– δ 133.10

d – δ 26.59



A total of four (4) types of proton atoms, six (6) types of carbon atoms, and a molecular weight of 120 g/mol were obtained in the compound by ^{1}H-NMR, ^{13}C-NMR and GC-MS. The spectral data of FT-IR, ^{1}H-NMR, and ^{13}C-NMR are compatible with the structure of this compound shown below:



Acetophenone

iv) Mass Spectrum of Acetophenone

The acetophenone was bombarded with a high electron beam in the first step, resulting in the formation of a molecular ion. The alkyl group was then removed from the molecular ion, resulting in the formation of phenyl acylium ion. Secondary fragmentation of this phenyl acylium ion results in the loss of carbon monoxide, resulting in the formation of phenyl ion. In the mass spectrum, this peak appears more prominently. As a result, this was the base peak in the mass spectrum.

Mass Spectrum of Acetophenone

Molecular weight: 120 g/mol
Base peak: 77 g/mol

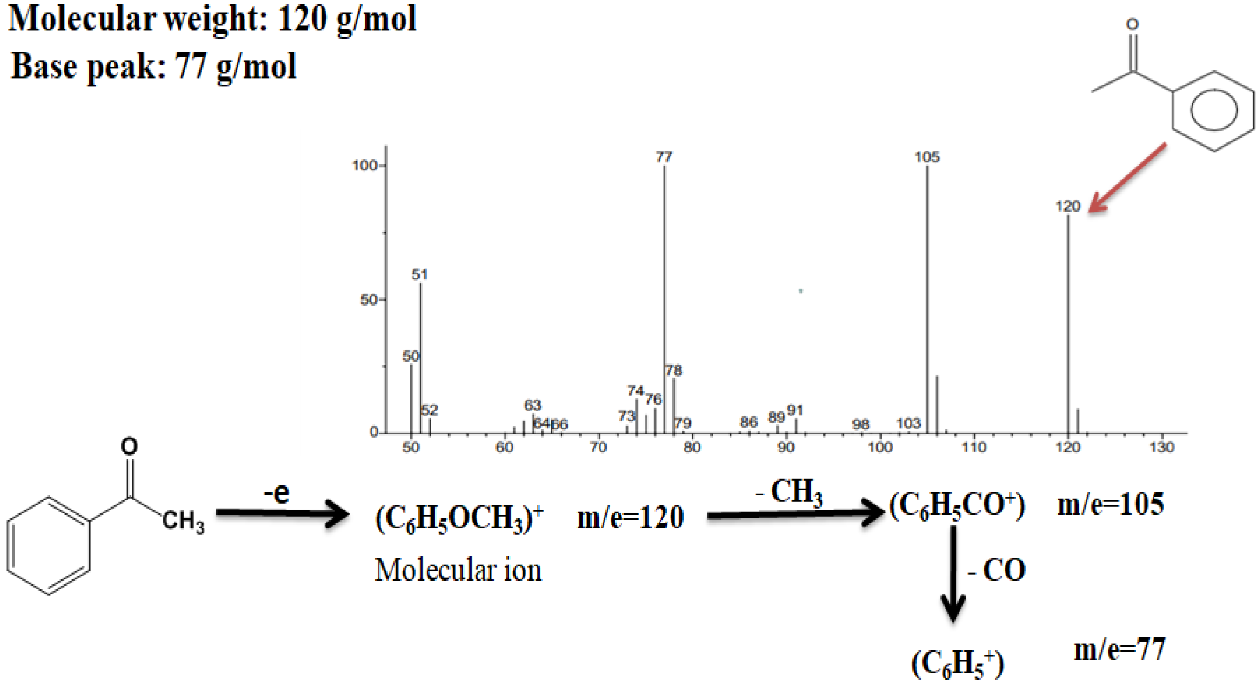


Figure.3.5.2: Mass spectrum of Acetophenone

IR Spectrum of Acetophenone

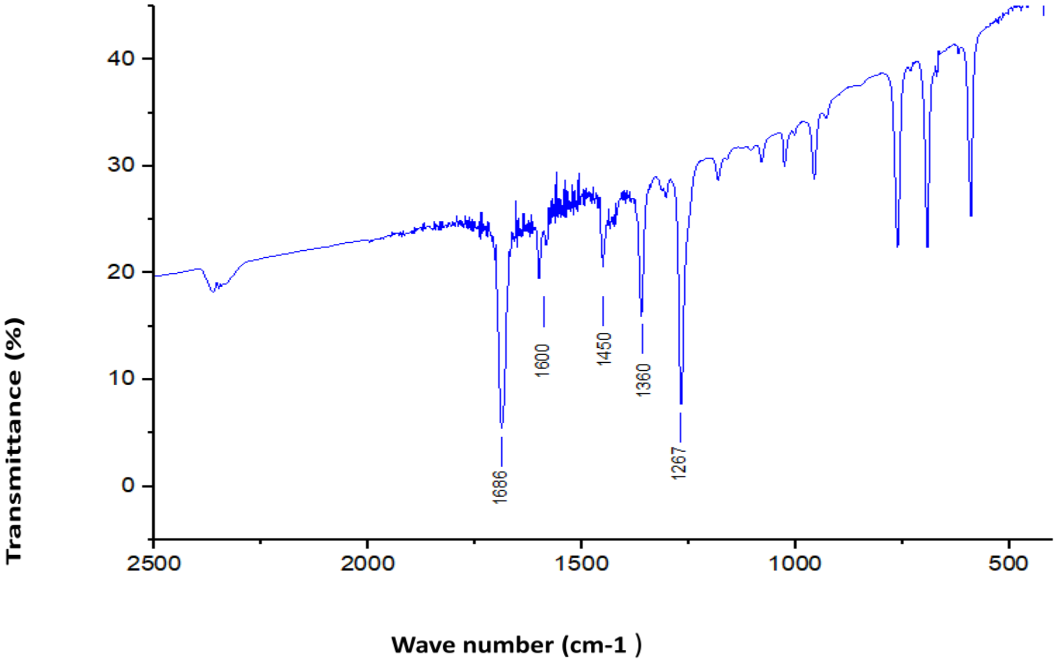


Figure.3.5.3: IR spectrum of Acetophenone

^{1}H-NMR Spectrum of Acetophenone

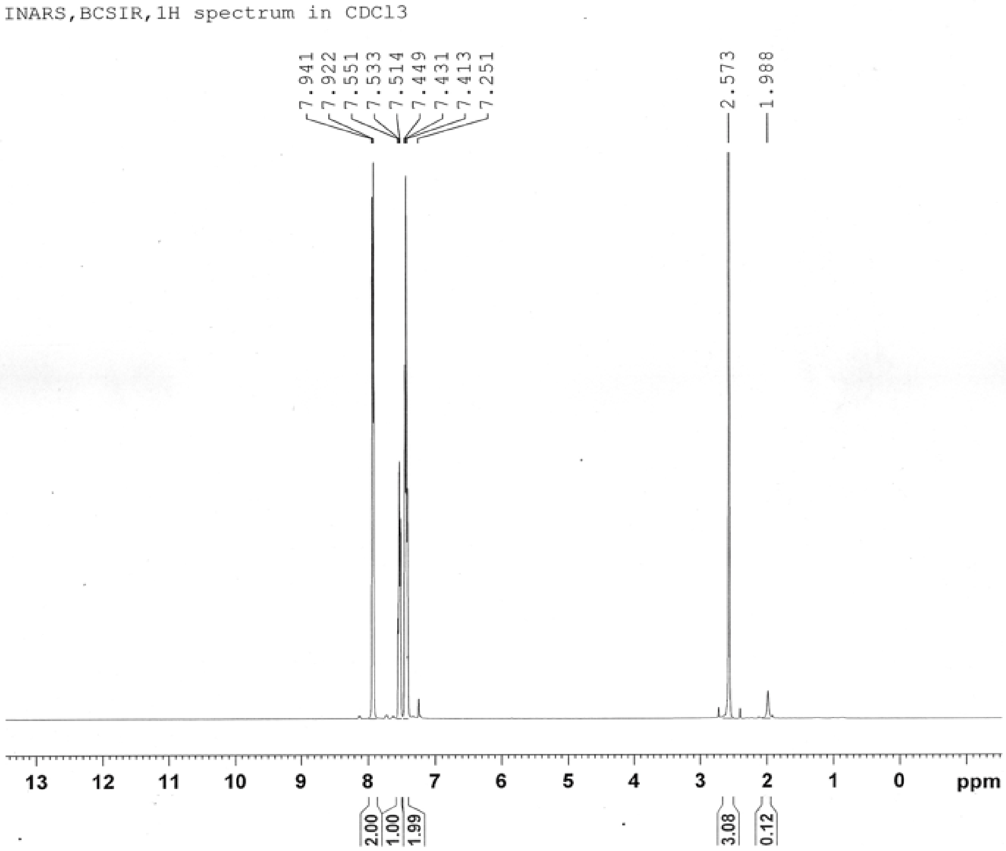


Figure.3.5.4:^{1}H-NMR Spectrum of Acetophenone

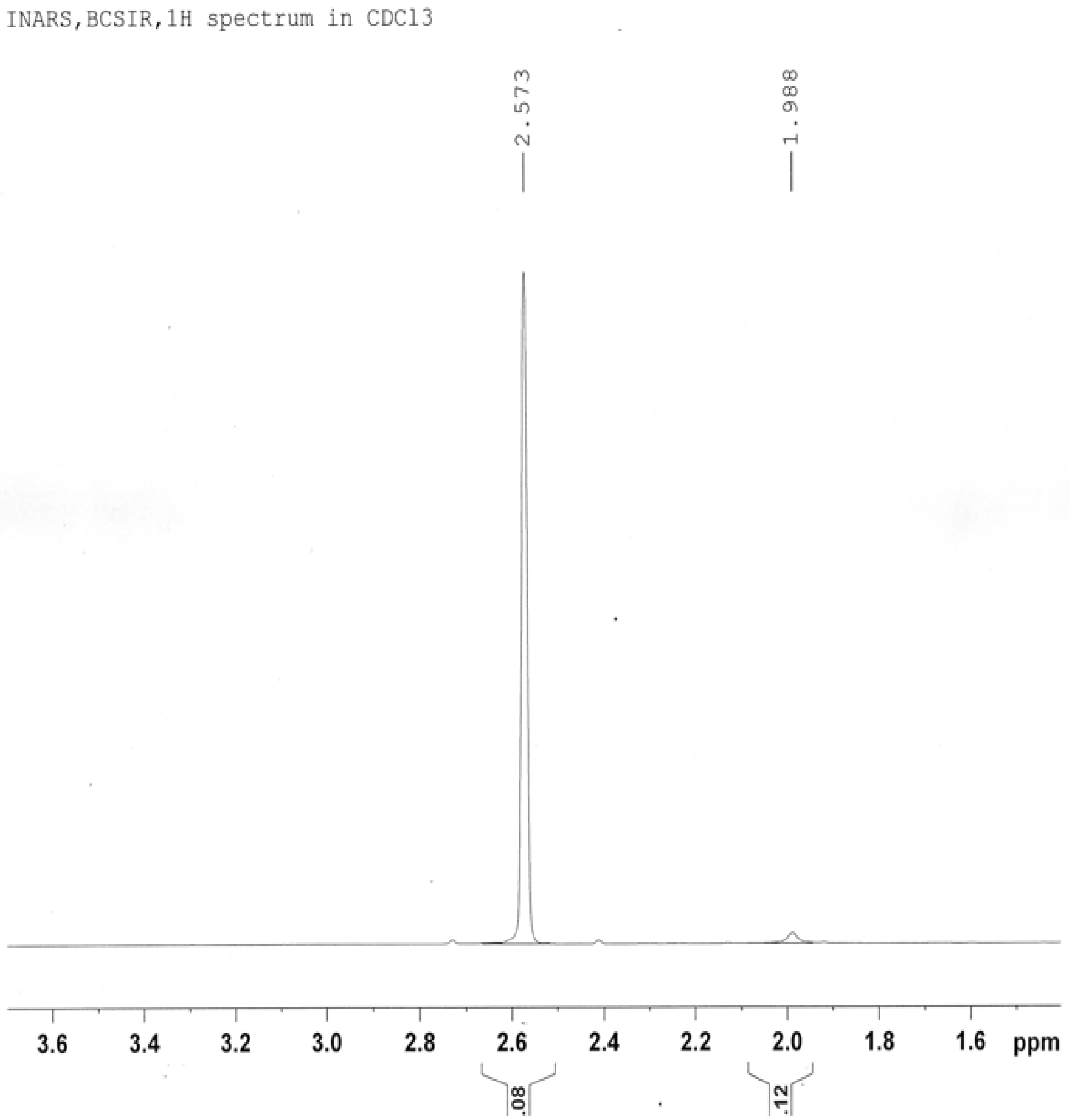


Figure.3.5.5:^{1}H-NMR Spectrum of Acetophenone

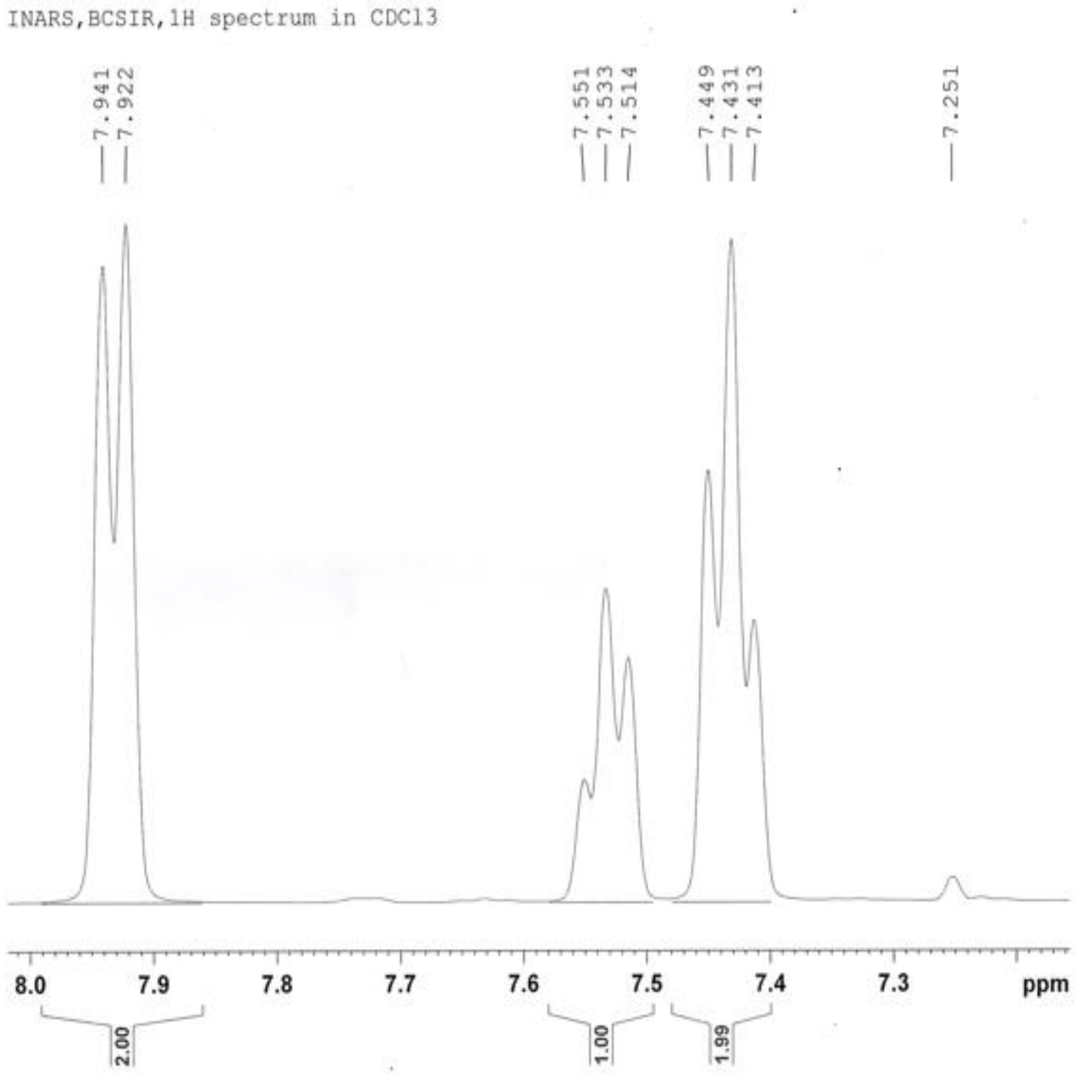


Figure.3.5.6:^{1}H-NMR Spectrum of Acetophenone

^{13}C-NMR Spectrum of Acetophenone

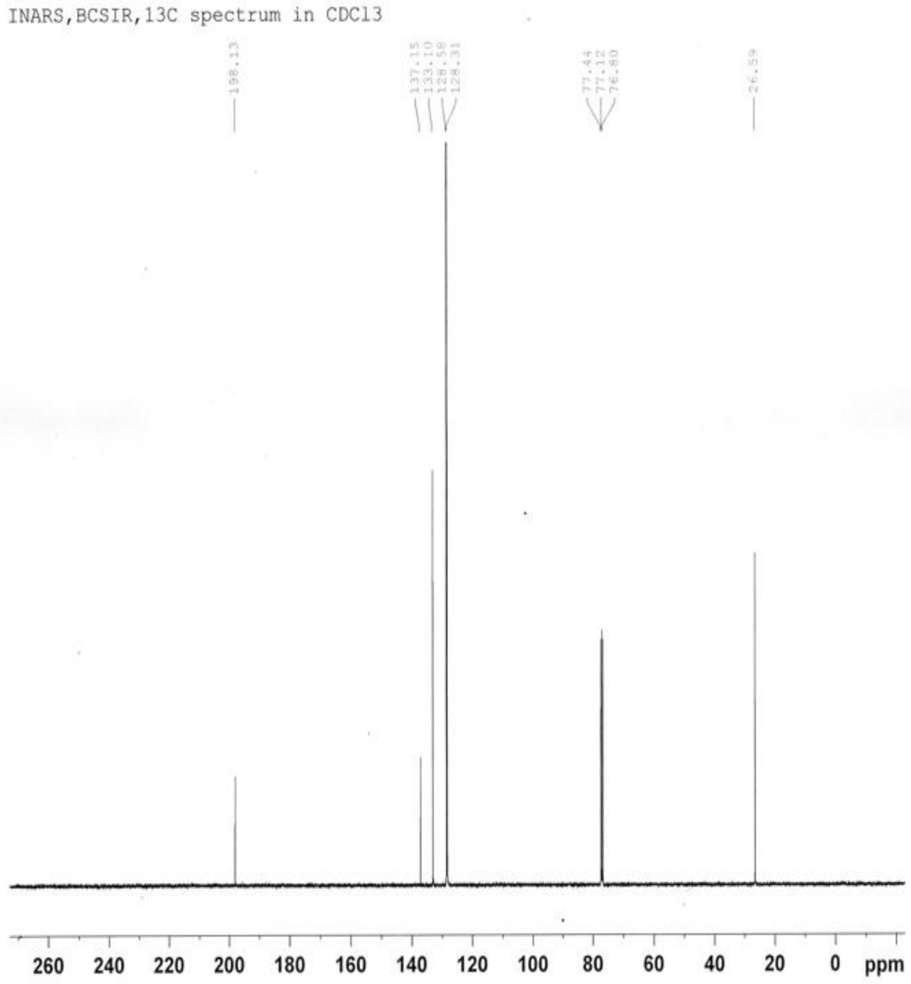
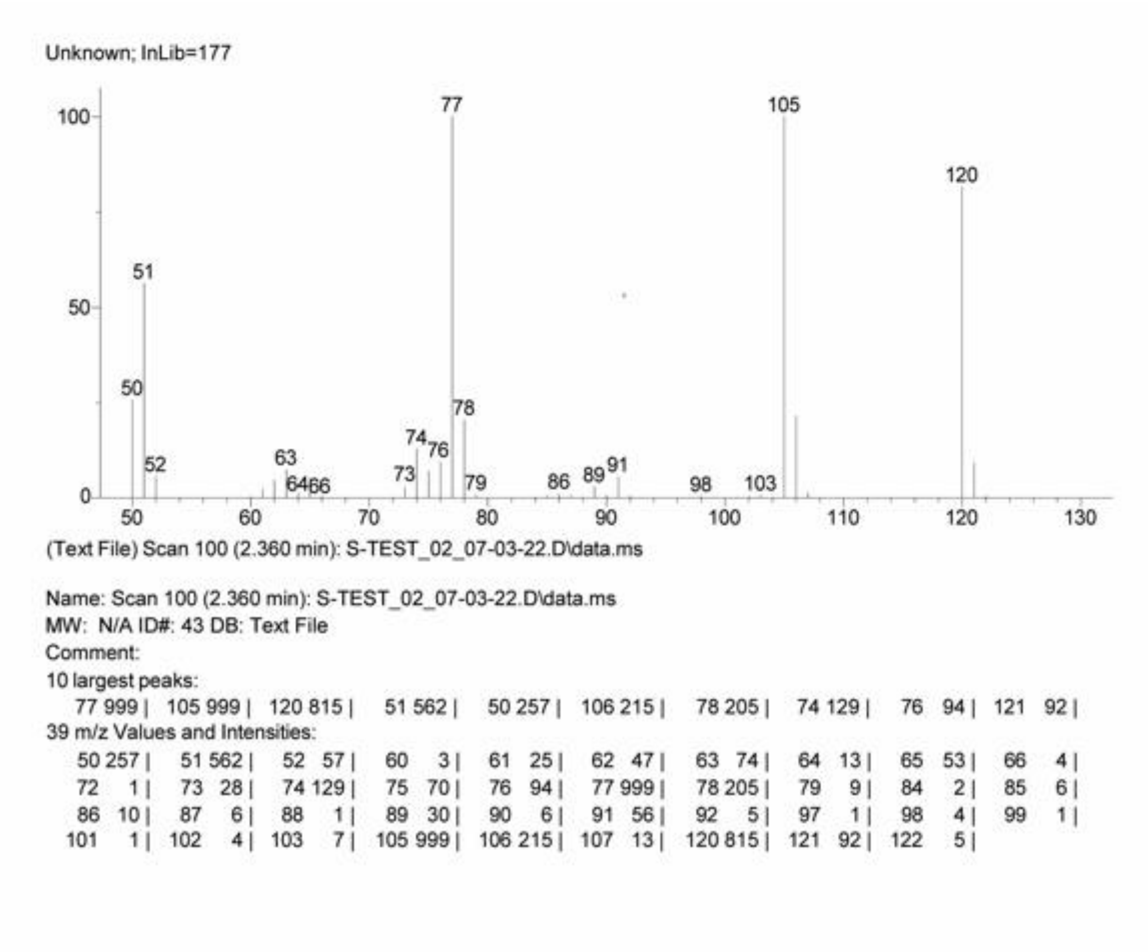


Figure.3.5.7:^{13}C-NMR Spectrum of Acetophenone



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Unknown; InLib=177

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Name: Scan 100 (2.360 min): S-TEST_02_07-03-22.D\data.ms
MW:  N/A ID#: 43 DB: Text File
Comment:
10 largest peaks:
   77 999 |  105 999 |  120 815 |    51 562 |    50 257 |  106 215 |    78 205 |    74 129 |    76   94 |  121   92 |
39 m/z Values and Intensities:
   50 257 |    51 562 |    52   57 |   60     3 |   61   25 |   62   47 |   63   74 |   64   13 |   65   53 |   66     4 |
   72     1 |    73   28 |    74 129 |   75   70 |   76   94 |   77 999 |   78 205 |   79     9 |   84     2 |   85     6 |
   86   10 |    87     6 |    88     1 |   89   30 |   90     6 |   91   56 |   92     5 |   97     1 |   98     4 |   99     1 |
  101     1 |  102     4 |  103     7 |  105 999 |  106 215 |  107   13 |  120 815 |  121   92 |  122     5 |
```

Figure.3.5.8: Mass spectrum of Acetophenone

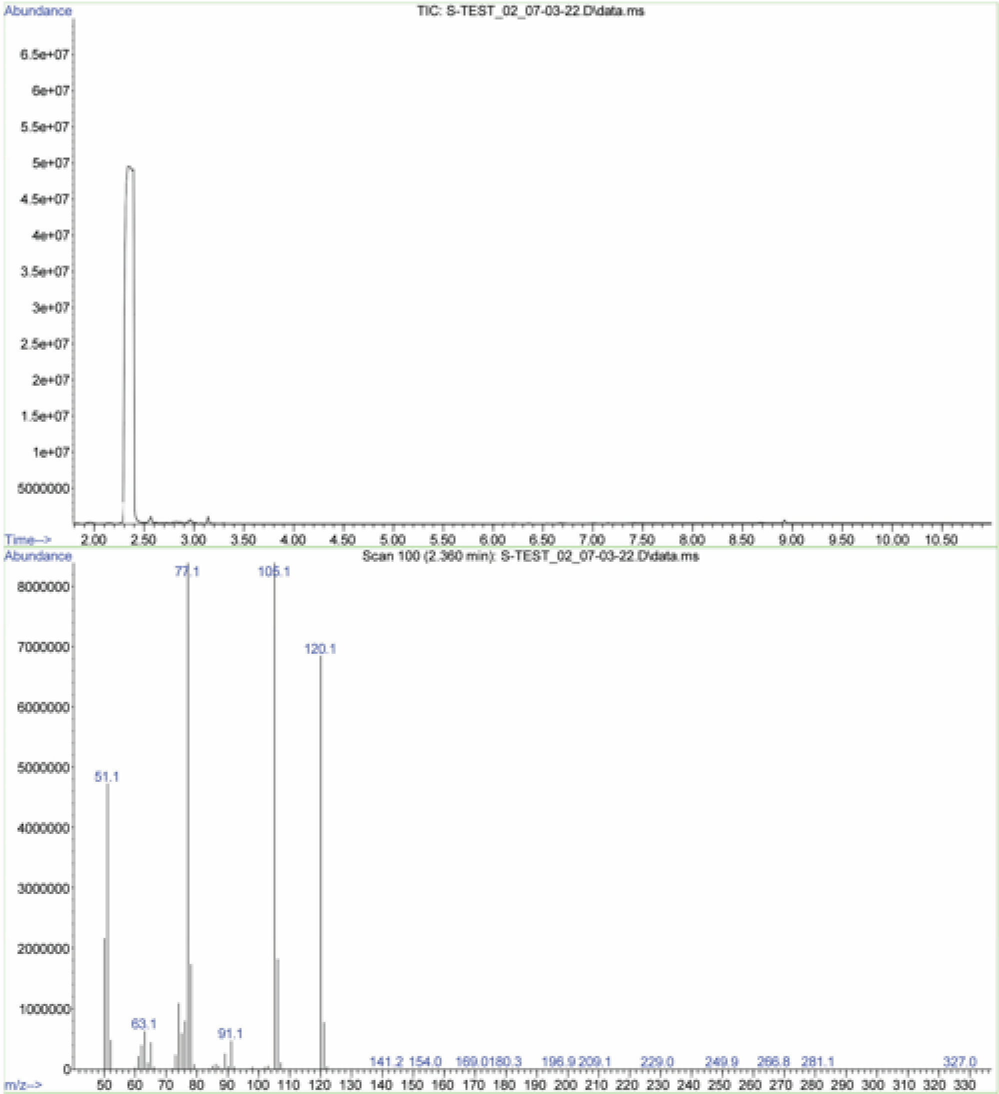

Figure.3.5.9: Mass spectrum of Acetophenone

3.5.4. Summary

The summary of the synthesized ketone is given below:

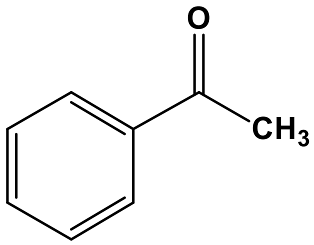

Figure.3.5.10: Structure of Acetophenone

- The synthesized acetophenone is used as a solvent in manufacturing of plastics and resins.
- pesticide, agrochemicals,
- polymers and synthetic chemistry

3.5.5. Possible Reaction Mechanism for Ketone Synthesis

Synthesis of ketones from secondary alcohols in the dehydrogenation reaction. In this method at first step forms the carbo anion by adsorbing one hydrogen atom from the O-H bond in 1-phenyl ethanol. By removing hydrogen gas in the second step, when the nickel plus ion adsorbs another hydrogen atom from the C-H bond to create Acetophenone.

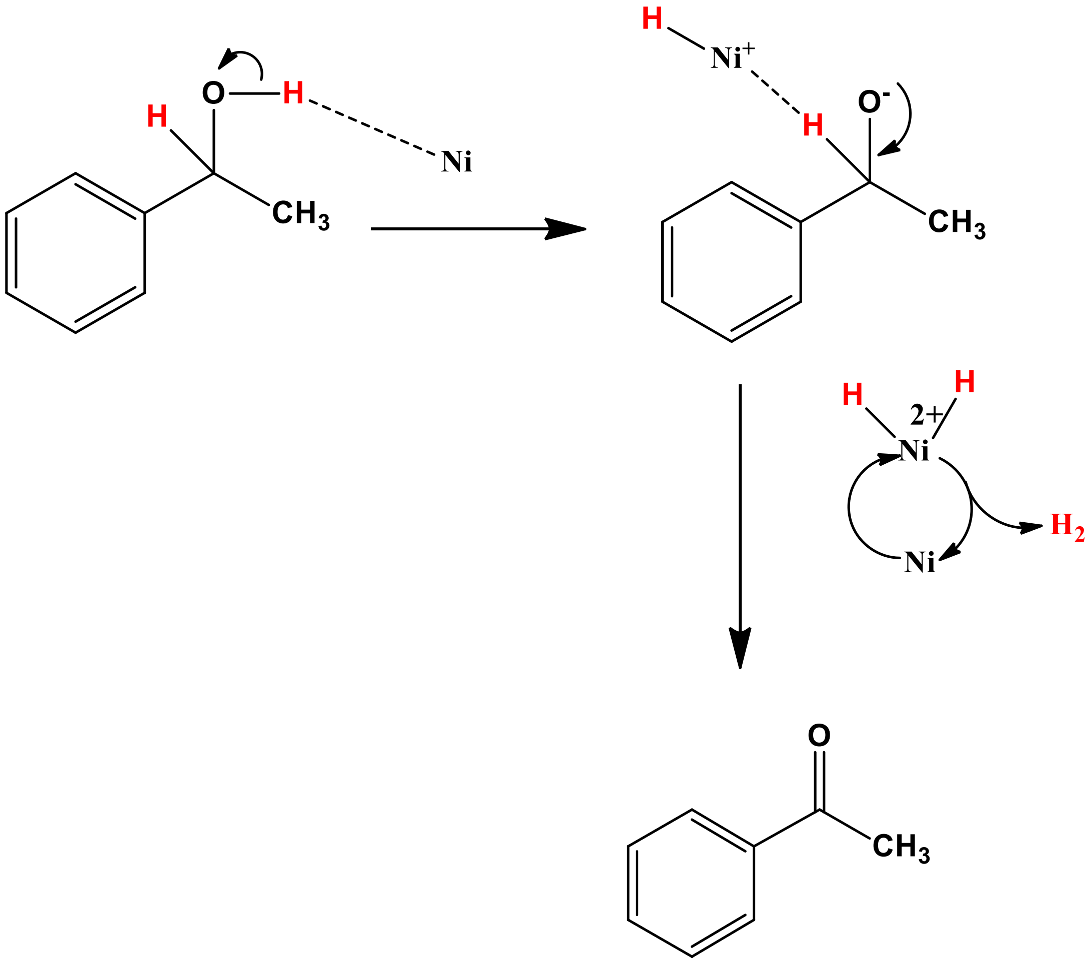

Figure.3.5.11: Possible reaction mechanism for ketone synthesis

Chapter 4

Conclusions

4.1. Conclusions

Finally, it was demonstrated that Ni/AC catalyst may be used as a heterogeneous catalyst for the synthesis of ketones from secondary alcohols. Using Ni/AC catalyst, seven same ketones were produced from 1-phenyl ethanol. These synthetic ketones have applications in medicine, pesticides, agrochemicals, polymer chemistry, and synthetic chemistry.

Since there is no particular method for the synthesis of ketones in presence of heterogeneous Ni/AC catalyst. Thus, it is said that a novel, multipurpose and endurable method for synthesis of ketones from secondary alcohols using Ni/AC catalyst as a reusable, affordable, and commercially available heterogeneous catalyst was established. This atom economical and facile method will provide an applied and expedient route for the synthesis of ketones from readily available starting materials.

Here, it can be concluded that the first common catalytic method of ketone synthesis from secondary alcohol uses Ni/AC catalyst as an efficient heterogeneous catalyst.

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