

“Phenol Hydrogenation / Hydrodeoxygenation Over Ni doped ZSM-5 in methanol-water system”

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Dissertation Submitted in Partial Fulfilments of the Requirements for the
degree of

**MASTER OF SCIENCE
IN
CHEMISTRY (CHE)**

Submitted by
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2015-2016

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CERTIFICATE

This is to certify that the project entitled “**Phenol Hydrogenation / Hydrodeoxygenation Over Ni doped ZSM-5 in methanol-water system**” submitted by Ravi Kiran in partial fulfilment of the requirement for the award of Master of Technology in Chemistry, VNIT, Nagpur is a record of students own work carried out by him under my guidance and supervision.

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CERTIFICATE

Forwarded here with the thesis entitled “**Phenol Hydrogenation / Hydrodeoxygenation Over Ni doped ZSM-5 in methanol-water system**” this thesis is being submitted by **Ravi Kiran** in partial fulfilment of the requirement for the award of **Master of Science in Chemistry, VNIT, Nagpur** is a record of students own work carried out by him under my guidance and supervision.

The matter embodied in this dissertation is original and has not been submitted to any other institute for the award of any degree.

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DECLARATION

This dissertation is submitted for the award of degree of **Master of Science (Chemistry)** at VNIT, Nagpur.

The work reported herein was carried out under the supervision of **Dr. J. D. Ekhe** during the period 2015-2016.

To the best of my knowledge, this work is original, except where suitable references were made to previous work. Neither this, nor any substantially similar dissertation has been submitted for any degree, diploma or qualification at any other university or institution.

(Submitted by)
Ravi Kiran

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(Ravi Kiran)

ABSTRACT

Continuously increased consumption of fossil fuels, decreased availability of easily accessible fossil fuels, significant contributions to climate change and wildly fluctuating fuels prices have combined to challenge the reliability and sustainability of our current energy source. A possible solution to this energy challenge is to develop new technologies to convert abundant biomass such as lignocellulosic materials into energy products in a cost-effective and environmentally friendly manner.

Biomass utilizes carbon dioxide and sunlight to synthesize organic molecules. One such part of biomass is lignocellulosic material, a waste material from pulp and paper industry which on depolymerisation give phenolic monomer units which can be further processed into useful bio chemicals or bio fuels. It is necessary to study the lignin model compound to optimize reaction conditions before applying them to complex system derived from biomass. This work preliminary focuses to find out the optimum reaction conditions for lignin model compounds like phenol for its reduced value added chemicals over Ni-ZSM-5 catalyst.

In this work, Catalyst H-ZSM-5 is synthesized with different precursors and reactions were performed with well characterized catalyst on batch type reactor (PARR reactor). APR (aqueous phase reforming) in methanol-water solvent system is used to generate Hydrogen for phenol hydrogenation / hydrodeoxygenation and reaction parameters such as temperature, solvent ratios (water to methanol), catalyst dose and time for reaction were investigated and evaluated using GC-FID after extracting the reaction mixture in Dichloromethane and results were reported in terms of % phenol conversion. Very high conversions of phenol (90%) to reduced products like cyclohexane and cyclohexanol is achieved at low temperatures near 67°C using 1:10 molar ratio of phenol to methanol with solvent (water – methanol) 1:1 ratio in 1 hour. Optimized conditions for highest conversion may be employable to phenols generated during application to potential raw material, lignin.

Thus the findings ensure that at low temperature without using gaseous hydrogen very high degree of phenol conversion is possible and they may be employable to more complex system like depolymerized products of lignin.

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CHAPTER 1: INTRODUCTION

The optimized reaction condition for phenol hydrogenation / hydrodeoxygenation over Ni-ZSM-5 catalyst is necessary to employable for more complex system derived from biomass to produce value added chemicals. In this contrast, it is important to know about biomass in general.

1.1 Biomass and Bio based Chemicals

Biomass is all biologically-produced matter based on carbon, hydrogen and oxygen. Humans have harnessed biomass-derived energy since the time when people began burning wood to make fire. Even today, biomass is the only source of fuel for domestic use in many developing countries. The estimated biomass production in the world is about 105 billion metric tons of carbon per year, about half in the ocean and half on land. Wood remains the largest biomass energy source today; examples include forest residues (such as dead trees, branches and tree stumps), yard clippings, wood chips and even municipal solid waste.



Figure 1.1 Different Sources of Biomass

Wood energy is derived by using lignocellulosic biomass (second-generation biofuels) as fuel. Harvested wood may be used directly as a fuel or collected from wood waste streams.

The largest source of energy from wood is pulping liquor or "**black liquor**," a **waste product from processes of the pulp, paper and paperboard industry**.

In the second sense, biomass includes plant or animal matter that can be converted into fibers or other industrial chemicals, including biofuels.

Industrial biomass can be grown from numerous types of plants, including miscanthus, switchgrass, hemp, corn, poplar, willow, sorghum, sugarcane, bamboo, and a variety of tree species, ranging from eucalyptus to oil palm (palm oil).

Based on the source of biomass, biofuels are classified broadly into two major categories.

First-generation biofuels: are derived from sources such as sugarcane and corn starch. Sugars present in this biomass are fermented to produce bioethanol, an alcohol fuel which can be used directly in a fuel cell to produce electricity or serve as an additive to gasoline. However, utilizing food-based resources for fuel production only aggravates the food shortage problem.

Second-generation biofuels: utilize non-food-based biomass sources such as agriculture and municipal waste. These biofuels mostly consist of lignocellulosic biomass, which is not edible and is a low-value waste for many industries. Despite being the favored alternative, economical production of second-generation biofuel is not yet achieved mainly due to chemical inertness and structural rigidity of lignocellulosic biomass.

That's why Catalyst are crucial for lignocellulosic biomass degradation and conversion into value added chemicals.

The biomass itself may be broken down into three basic categories

Carbohydrates, lignin and fats/oils. Carbohydrates primarily include cellulose and hemicelluloses fractions. Fats are mainly comprised of triglycerides and fatty acids. A simple diagram showing renewable fuels production from biomass is provided in Fig. (1.2)⁽¹⁾

Hydrocarbon based energy carriers from biomass requires new catalytic approaches to transform the wide variety of substrates into a uniform pool of hydrocarbons. Above mentioned reasons developed interest in lignin derived resources. Bio-oils produced from lignocellulose biomass contains over 400 different chemical compounds contains a substantial

concentration of phenolic compounds and novel routes has been already devised to convert them into C₆ – C₉ gasoline range hydrocarbons but yields and selectivity is not satisfactory yet.

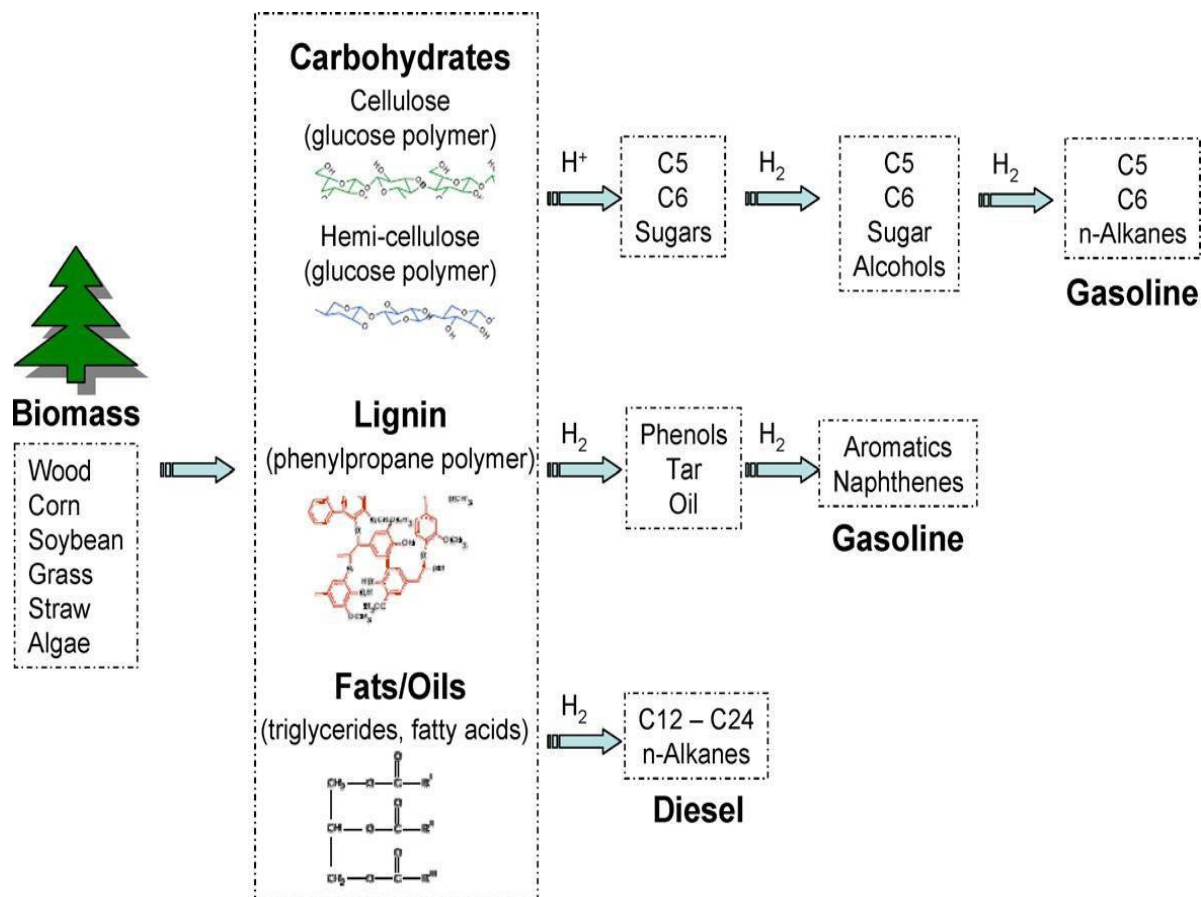


Figure 1.2 Hydrodeoxygenation of the basic building blocks of biomass to renewable hydrocarbon fuels.

1.2 Lignocellulosic biomass: A potential sustainable source

Lignocellulosic biomass is the feedstock for the pulp and paper industry. This energy-intensive industry focuses on the separation of the lignin and cellulosic fractions of the biomass. It is the most abundantly available raw material on the Earth for the production of bio-fuels, mainly bio-ethanol. It is composed of carbohydrate polymers (cellulose, hemicellulose), and an aromatic polymer (lignin). These carbohydrate polymers contain different sugar monomers (six and five

carbon sugars) and they are tightly bound to lignin. Lignocellulosic biomass can be broadly classified into virgin biomass, waste biomass and energy crops. Virgin biomass includes all naturally occurring terrestrial plants such as trees, bushes and grass. Waste biomass is produced as a low value byproduct of various industrial sectors such as agricultural (corn stover, sugarcane bagasse, straw etc.), forestry (saw mill and paper mill discards). Energy crops are crops with high yield of lignocellulosic biomass produced to serve as a raw material for production of second generation biofuel examples include switch grass (*Panicum virgatum*) and Elephant grass.

During annual production 100 million metric of wood pulp is obtained worldwide, about 2 million metric of Kraft lignin is also generated per year. Lignosulfates has many applications such as adhesives, adsorbent, sensors in sensitization, various polymerizing blends in industry. For example, as of 2004, the pulp and paper industry alone produced 50 million tons of extracted lignin, yet the existing markets for lignin products remain limited and focus on low value products such as dispersing or binding agents. As a result, only approximately 2% of the lignin available from the pulp and paper industry is used commercially with the remainder burned as a low value fuel. Nevertheless, lignin conversion has significant potential as a source for the sustainable production of fuels and bulk chemicals. With its unique structure and chemical properties, a wide variety of bulk and fine chemicals, particularly aromatic compounds, as well as fuels are potentially obtainable from lignin. Indeed, lignin can be regarded as the major aromatic resource of the bio-based economy. The pulp and paper industry produced lignin of around ten millions metric per year. Mechanical wood pulp produce in the yield of about 90-98 % with the retention of lignin, were generally used to make low quality newsprint, telephone directories, because of light induced photo-oxidation of lignin and yellowing of the papers.

After delignification, the lignin undergoes structural changes. Lignin is one of the natural abundant polymers which are expected to play an important role in the production of bio-products. Large amount of lignin is produced by pulp and paper industry every year. The large amount of degraded lignin is used in low value products and energy production. The chemical industry uses half of the pulp material for paper making and remaining half lignin is used as source of energy.

1.3 Lignin Structure

Lignin is a natural polymer obtained from wood. It mainly consists of three phenyl propane units namely p-coumaryl, coniferyl and sinapyl alcohol. It is kind of net liked structure with phenyl propane units linked to each other by various linkages². These phenyl propane (C9 or C3-C6) units are the main building blocks of the structure of lignin (Fig.1.3). These three monolignol are interconnected with each other by different linkages such as β -O-4, β - β , β -5, β -1, α -O-4, 5-5 and dibenzodioxocin³. Of all linkages shown above, β -O-4 linkage is found abundantly in the structure of lignin. The lignin structure mostly consists of etherified and semi-etherified linkages. Around 40- 60% of the linkages are by β -O-4 bond, different types of linkages for lignin a set of three dimensional structures which is very tough for depolymerisation. Hence, it provides great strength to cell walls to protect from outer environment.

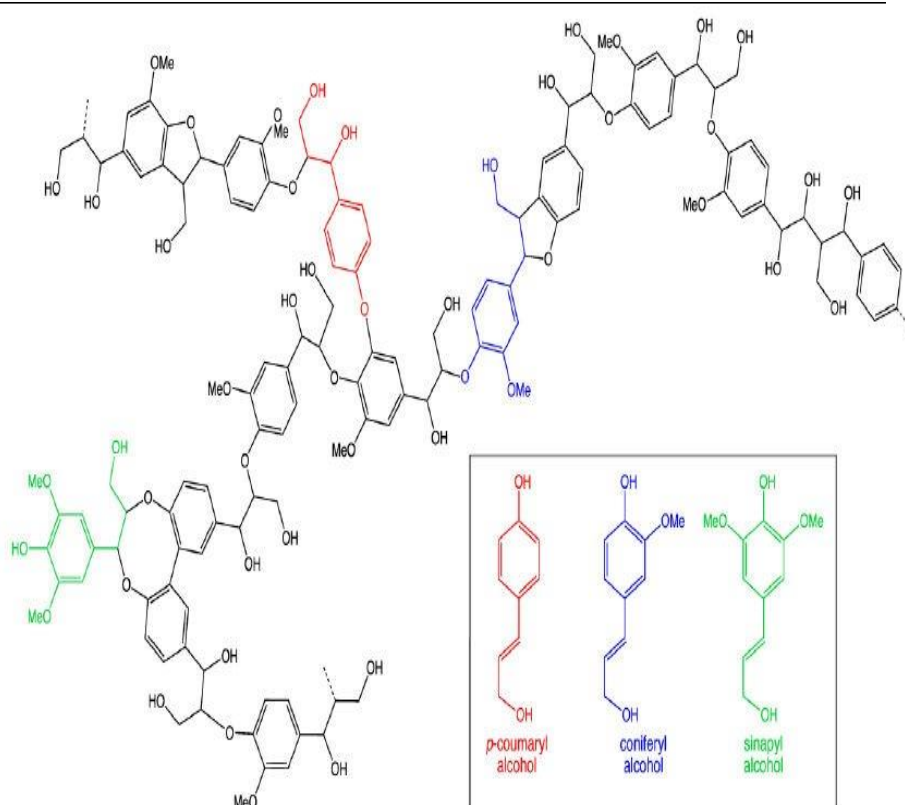


Figure 1.3 Structure of Lignin and phenolic monomers derived after depolymerisation.

1.4 Initial Screening of lignin derived products

Many possibilities for products from lignin and the various real or theoretical technologies required to make lignin-derived products. Identifying products from lignin was more challenging because of lignin's complex nature as a feed. Often, rather than listing discrete chemicals, classes of chemicals were identified based on functionality. Nevertheless, more than 50 opportunities were catalogued.

The possible products were evaluated on the basis of a combination of fit with currently available technology for their use, likely acceptance in the products marketplace (known market or unknown market) and an assessment of the degree of difficulty to develop the technology. The compounds were scored as high, medium, or low using the following criteria:

Technology degree of difficulty – this evaluation assessed the potential number of steps required and the relative difficulty of achieving those steps. For many of these compounds, there is little or no existing industrial experience or process evaluation history to draw on. The assessment for this criterion was made based on available information from the open literature, evaluation of the potential process by the team, and other experts as necessary.

Market – this criterion evaluated both potential market size and expected product value using standard reference sources such as the *Chemical Economics Handbook*.

Market risk – this criterion evaluated the potential risk of bringing a given lignin-derived product into the market. An example of a risk considered “low” would be the introduction of a lignin-based source of BTX or syngas. A risk considered “high” included compounds currently not recognized as chemical building blocks or products that would likely be produced as mixtures.

Building block utility – this criterion assessed the potential of a candidate compound to serve as a starting material for a larger group of derivatives.

Mixture – this criterion assessed whether a candidate could be derived from lignin as a single compound or whether it would be present as a complex mixture.

Table 1.1 Products Potentially Derived from Lignin Conversions

Lignin Derived Product	Current Technology Status from Lignin*	Expected Difficulty from Lignin*	Market Volume*	Market Value [†]	Market Risk*	Utility as Building Block*	Expected from Lignin as Mixture?
Syngas Products							
Methanol/Dimethyl ether (DME)	H	L	H	\$0.80/gal	L	H or Fuel	Y
Ethanol/mixed alcohols	L	H	H	\$1 - \$3.5/gal	L - M	H or Fuel	Y
Fischer Tropsch Liquids	H	L	H	\$1.5 - \$2/gal	L - M	L	Y
Mixed Liquid Fuels	M	M	H	\$1.3 - \$2/gal	L	L	Y
Hydrocarbons							
BTX and Higher Alkylates	L – M	M		\$2/gal	L	H	Y
Cyclohexane	L	M	H	\$2.20/gal	L	M	Y
Styrenes	L	M-H	H	\$0.70/lb	?	?	?
Biphenyls	L	H	L - M	?	?	L	Y?
Phenols							
Phenol	L-M	M	H	\$0.55 - \$0.65/lb	L	H	N
Substituted Phenols			M	\$0.70 - \$2.00/lb	M	M	Y
Catchols, cresols, resorcinols	L	H		>\$1.5/lb	?	M	Y
Eugenol	L	H	?	M-H	?	?	Y

Products Potentially Derived from Lignin Conversions (Continued)

Lignin Derived Product	Current Technology Status from Lignin*	Expected Difficulty from Lignin*	Market Volume*	Market Value [†]	Market Risk*	Utility as Building Block*	Expected from Lignin as Mixture?
Syringols	L	H	?	M-H	?	?	Y
Coniferols	L	H	?	M-H	?	?	Y
Guaiacols	L	H	?	M-H	?	?	Y
Oxidized Products							
Vanillin	H	L	L	\$5.90/lb	H	L	N
Vanilic Acid	M	M	?	?	H	?	?
DMSO	H	L	M	<\$1/lb	H	L	N
Aromatic Acids	L	H	H	\$0.40 - \$0.50/lb	L	H	Y
Aliphatic Acids	L	H	H	\$0.45 - \$0.65/lb	L	M-H	Y
Syringaldehyde and Aldehydes	L	H	?	?	M-H	M	Y
Quinones	L	H	L-M	> \$1/lb	?	L	?
Cyclohexanol/al	L	H	H	> \$0.75/lb	L	H	Y
Beta keto adipate			?	?	H	M	?
Macromolecules							
Carbon Fiber	L – M	M – H	H	ACC Target * = \$3 - \$5/lb	M	L	N
Polyelectrolites	L – H	M	M	\$1.5 - \$3/lb	M-L	M	Y
Polymer Alloys	L – M	M	?	\$1 - \$2/lb	M	NA	Y
Fillers, Polymer Extender	M	H	M	< \$1/lb	M - H	NA	Y
Substituted Lignins							
Carbonylated	L	H	?	?	M - H	?	Y

Ethoxylated	L	M	L	\$1.50 – 2.50	M - H	?	Y
Carboxylated	L	M	L	\$1.50 – 2.50	M - H	?	Y
Epoxidized	L	H	?	?	M - H	?	Y

*H=High or well Developed

M=Moderate or Partial development

L=Low, or Emerging, Requires Intensive Effort for Development

?= Unknown or insufficient

Information NA=Not Applicable

+Prices are 2005 or mid-2006 where available

++ Gasification technology is dependent on lignin source and in some cases the technical feasibility can be high, for example gasifying black liquor will have a different set of difficulties than other lignin containing fractions.

1.5 Lignin depolymerisation:-Phenolic monomers

Lignin is a high molecular weight polymer composed of methoxylated alkylphenol units. Accordingly, it can be regarded as a rich source of phenols. However, because lignin has a random, three-dimensional network, it is difficult to decompose lignin into phenols. Various methods for the production of phenols from lignin have been investigated (Fig. 1.5), such as hydrolysis pyrolysis, alkaline oxidation and hydrocracking. Among these methods, hydrocracking process usually gives good results with respect to the yield of phenols. Because biomass including lignin contains a lot of oxygen, hydrodeoxygenation (HDO) reactions occur during hydrocracking, where oxygen in biomass is removed and converted into H₂O. In Recent times, HDO of biomass-derived feeds such as bio-oils, lignin and lignin model compounds has been widely studied and it is identified as a prospective route for production of biofuels by conversion of biomass into bio-oil through flash pyrolysis followed by upgrading via HDO.

Flash pyrolysis is advantageous in making a locally produced liquid that minimizes transportation costs to larger biorefineries. However, bio-oil is a viscous, polar, and acidic liquid with a low heating value, making it, in most cases, unsuitable as an engine fuel directly. These unfavorable characteristics are all associated with high levels of water (10–30 wt %) and oxygen containing organic compounds (30–40 wt % oxygen) in the oil. In HDO, bio-oil

is treated with hydrogen at a pressure of up to 200 bar and temperatures in the range from 200 to 400 °C. This converts the oxy compounds to a hydrocarbon product that is separated from the water and ultimately gives a product equivalent to crude oil.

Identifying lignin as a rich resource of phenols our work aims for the effective conversion of phenols to hydrocarbons and other useful products.

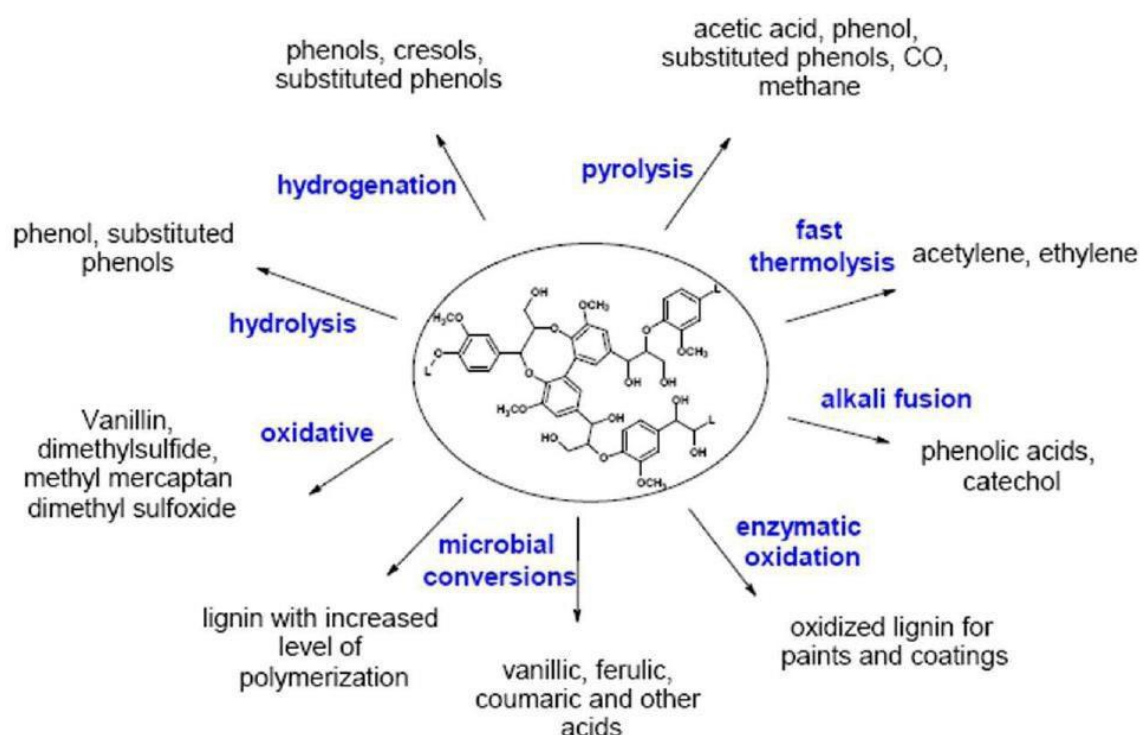


Figure 1.5 Various possible uses of chemical processing of lignin

1.6 Why phenol study?

Lignin has large amount of phenol hidden in it. When only degraded, it can recombine to form other more stable compounds. In this connection it is important to prevent it recombining ability. It can be done by hydro-deoxygenation. This justifies the selective approach to study a sample molecule phenol. The base of all phenolic compounds is phenol, which is highly reactive in the synthesis of phenolic resins. Other monomeric phenolic compounds (or simple phenols) in bio-oil, such as cresol and vanillin, are also very valuable chemicals. Oligomeric polyphenols contain varying numbers of functional groups, and constitute the majority of phenolic compounds contained within typical bio-oils. Oligomeric polyphenols (or pyrolytic lignin) can be used, for instance, in the synthesis of phenol resin. The concentrations of

phenolic compounds in bio-oil derived from non-catalytic biomass pyrolysis are strongly dependent on the kinds of biomass feedstock, pyrolysis operation conditions, and pyrolysis reaction systems.⁴

The commercial significance of the reaction of phenol with hydrogen is 2-fold⁵, that is, as a synthesis route and as a pollution abatement methodology. On one hand, the selective hydrogenation of phenol yields cyclohexanone, a key raw material in the production of both caprolactam for nylon 6 and adipic acid for nylon 66. Phenol is, on the other hand, an established environmental toxin⁶ and phenolic waste originates from a variety of industrial sources including oil refineries, petrochemical units, polymeric resin manufacturing, and plastic units.⁷ Thermal and/or catalytic oxidations are at present the widely favored pollution abatement techniques for treatment/disposal of such organic waste.⁸ However, effective incineration is energetically demanding and an incomplete combustion can generate highly toxic products.⁹ To minimize any negative environmental effects and conserve resources, the first abatement option that should be considered is the recovery and reuse of raw material. Catalytic hydrogenation/hydrogenolysis is now emerging as a viable alternative to destructive incineration whereby the hazardous substances are transformed into useful products⁽¹⁰⁻¹²⁾. This approach has relatively low-energy requirements and minimal toxic emissions, in short, a —best practicable environmental optional.

ϵ -Caprolactam is produced worldwide on one of the largest scales among commercial chemical products. Its preparation is typically carried out in a three-step procedure: Synthesis of cyclohexanone either by oxidation of cyclohexane or by hydrogenation of phenol in the gas phase or liquid phase, formation of cyclohexanone oxime and Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam. Because of the ever-increasing industrial demand for ϵ -caprolactam, extensive efforts have been devoted to maximizing the efficiency of each reaction step. For example, the development of an efficient catalyst for selective hydrogenation of phenol to cyclohexanone has received a great deal of attention in recent years. Phenol can be hydrogenated to cyclohexanone in a —one-step or a —two-step process. The two-step process involves hydrogenation of phenol to cyclohexanol, followed by dehydrogenation to cyclohexanone.

Cyclohexanol or alkyl-substituted cyclohexanols, and cyclohexanone are important intermediates in the synthesis of nylons 6 and 66, pharmaceuticals, fine chemicals, etc. These

compounds can be synthesized from the hydrogenation of phenol and alkyl- substituted phenols, besides the catalytic oxidation of cyclohexane¹³.

The various prospective of phenol studies lead our interest in studies of phenol hydrogenation and hydrodeoxygenation process for removing the oxygen content. Oxygen removal is an important step in biofuel upgrading that can be accomplished by different reaction paths such as dehydration, hydrogenation, and hydrogenolysis. Particular attention has been recently devoted to the upgrading of pyrolysis oils derived from lignocellulosic biomass. During the past few years, catalytic hydrodeoxygenation has been extensively investigated for a number of bioavailable precursors derived from the conversion of hemicellulose (branched polymers of different sugar monomers) and cellulose (i.e., unbranched polymers of glucose), which are embedded in the cell walls of plants.

Difficulties in Hydrogenation and Hydrodeoxygenation processes`

For efficient utilization of lignin derived phenolic compounds, various studies on phenol taking it as a model compound is performed. Lignin derived phenolic oil can lead to C12-C18 hydrocarbons by studying the selective hydroalkylation of phenols to cycloalkanes. Hydrogenation and Hydrodeoxygenation of phenol compounds are in interest, but existing methods have problems that can be identified as given below

1.7 Problems in phenol hydrogenation processes

Liquid phase catalytic hydrogenation is most useful, is of two types, hydrogenations of organic compounds via hydrogen-transfer or with H₂ gas.

For hydrogen-transfer hydrogenation, certain multi-atomic organic compounds containing hydrogen can serve as the hydrogen source in the presence of hydrogenation catalysts. Suitable donors include compounds, such as organic alcohols, hydrazines, organic acids and their salts. In general, apart from convenience, hydrogen-transfer reductions have no advantages over conventional hydrogenation. Oxidation of non- primary alcohols, the most commonly used hydrogen donors, to ketones is not an environmental-friendly procedure.

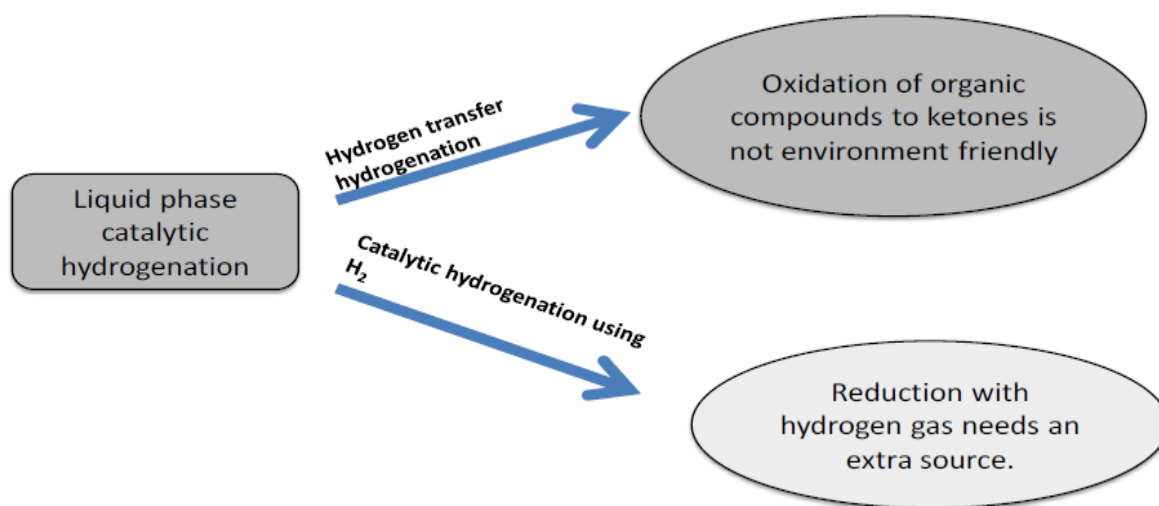


Figure 1.6 Aspects of liquid catalytic hydrogenation of phenol

Liquid phase catalytic hydrogenation using H_2 gas has been thought to be an environmentally benign method. In liquid phase catalytic hydrogenation procedure, organic reactants are reduced with H_2 gas into the products over Pt or Ni group metal catalyst in alcohol solvent. Therefore, an extra H_2 source is certainly needed.

A third approach for hydrogen production is based on the view of Prof. Dumesic from University of Wisconsin, who reported that H_2 could be produced from oxygenated hydrocarbons by **aqueous-phase reforming (APR)** under mild conditions (420—530 K) over catalyst of Pt, Raney Ni or Raney-Ni modified with Sn.

An example of APR is shown in figure 1.7 where a methanol water system is used for hydrogenation of nitrobenzene to aniline. An experimental data for hydrogenation product yield and selectivity is shown in table 1.2.

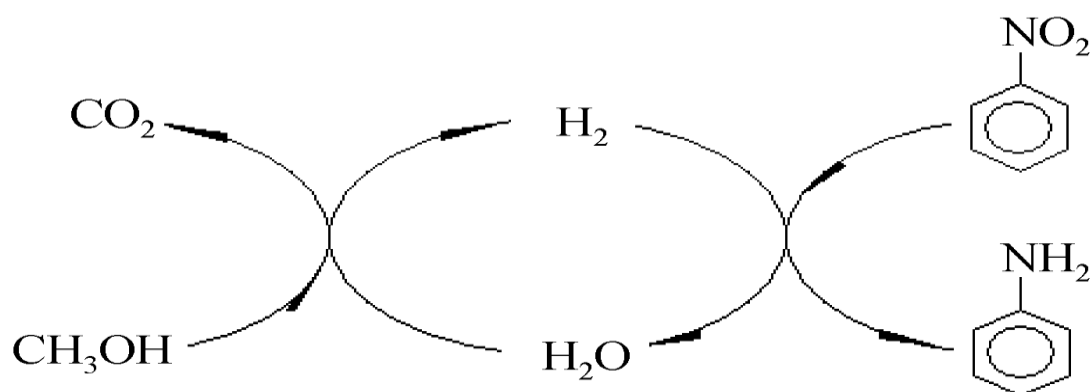


Table 1.7 APR of methanol-water system for hydrogenation of nitrobenzene¹⁴

These reactions may take place via formation of CO as an intermediate product, which is subsequently converted to CO₂ by water gas-shift reaction. Generations of H₂ and CO₂ by aqueous-phase reforming at low temperature, however, is accompanied by selectivity challenges, since the reaction of H₂ with CO or CO to form alkanes (C_nH_{2n+2}) is highly favorable at these low temperatures by methanation and Fischer Tropsch reactions.

Table 1.2 Experimental data for novel hydrolytic hydrogenation of phenol¹⁴

S.n	H ₂ O:methanol:phen	Conversio (%)	Selectivity (%)		
			cyclohexene	Cyclohexano	Cyclohexanon
1	0:100:1	82.27	0	54.1	32.6
2	40:20:01	80.4	0	85.49	14.51
3	20:05:01	31.66	0.65	69.84	29.52
4	40:05:02	83.32	1.97	81.62	16.4

1.8 Problems in Phenol Hydrodeoxygenation (HDO) process

HDO is an example of hydro processing application for the production of both renewable (“green”) gasoline and renewable (“green”) diesel. HDO reactions also occur during the hydro processing of petroleum fractions along with hydrodesulphurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM) and the saturation of olefins/aromatics. These hydroprocessing reactions use high pressure hydrogen to remove S, O and N heteroatoms out of petroleum feedstocks through a series of hydrogenolysis and hydrogenation steps. Major challenge with this concept is to find a suitable catalyst with high activity of deoxygenation reaction and at the same time obtain sufficient life time, as deposition of carbonaceous species has proven to be a severe problem.

1.9 Objectives of this research project

Problems needed to be addressed

(a) Solvent system problems

APR of alcohols for H₂ production is kinetically inhibited due to high activation barrier and is difficult to achieve due to energies of C-H (401 kJ mol⁻¹) and O-H (437.7 kJ mol⁻¹). MeOH as H₂ donor can be efficiently achieved in the presence of water under moderate

conditions (role of catalyst was found to be important). Solvent ratios can have profound effects on H₂ generation and Optimized solvent ratios are needed to be discovered for efficient conversions and selective product yields.

(b) Catalyst and dose

Need for HDO catalyst is to be relatively inexpensive and function at lower temperatures (<573K) to prevent coking. Various catalyst screening experiments have been performed and our quest aims for a common catalyst which can be used for lignin depolymerisation as well as hydrogenation and HDO. Ni/HZSM-5 is a recognized catalyst for depolymerization of lignin and found to give following pathways for HDO (Figure 1.8).

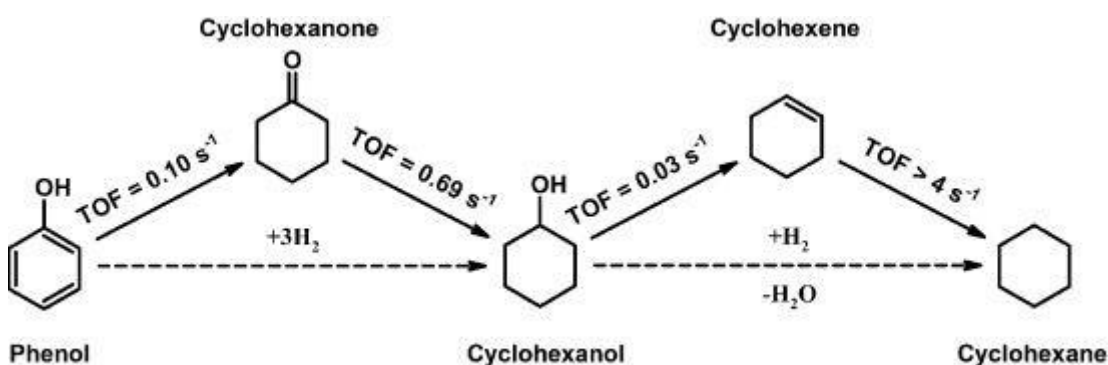


Figure 1.8 Pathways for HDO of phenol over Ni-HZSM-5, (TOF=turn over frequency)

(c) Temperature and time

Study the catalytic activity of Ni/ZSM-5 at various temperatures (<300 °C) and time

(1 hr-20 hr) on various catalytic doses for hydrogenation and HDO using PARR reactor. Study

the conversion and selectivity by analysing the extracted product on GC-MS/FID.

(d) GC Problems

Need to design GC program to get better peak separation from solvent peak.

Factors considered for the peak resolution, separation and identification.

- 1. Choice of Column on the bases of Products and Column temperature programming.*
- 2. Choice of carrier gas and its flow rate.*
- 3. Injector and Detector temperature.*
- 4. Choice of solvent.*

Aim of this project

By studying phenol Hydrogenation / HDO reactions similiar conditions can be developed for efficient conversion of lignin derived phenolic compounds to produce added biofuels. Methods can be developed for phenol resins, pharmaceutical industries and caprolactum synthesis.

2 CHAPTER 2: LITRATURE SURVEY

Phenol, which we are taking as a model compound exhibits single functionality. Phenol hydrogenation studies have attracted wide attentions because of the multiple utility mentioned in the introduction section. Most of these studies are performed using H₂ gas as hydrogen source and various catalyst screening studies have been done. Our work uses a novel liquid system for the source of hydrogen and choice of catalyst, temperature, time and catalyst doses are chosen from the previous literature survey available for phenol hydrogenation using H₂ gas as hydrogen source.

2.1 Hydrogen Source

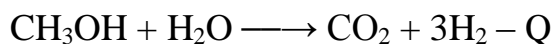
The two reported works,

Endothermic aqueous phase reforming of oxygenated organic compounds for H₂ production

Exothermic liquid phase hydrogenation of organic compounds,

are performed under same type of pressure and temperature conditions. This gave rise the idea of using a novel liquid system for catalytic hydrogenation where hydrogen can be produced by aqueous phase reforming of oxygenated hydrocarbons and can use this hydrogen in the hydrogenation reactions of desired organic compounds. The usage of active hydrogen generated from aqueous-phase reforming of oxygenated hydrocarbons for liquid catalytic hydrogenation of organic compounds could lead to increasing the selectivity to H₂ in the aqueous-phase reforming due to the prompt removal of hydrogen on the active centres of the catalyst¹⁴. This idea has many advantages like we can increase the selectivity of a specific desired product in the reaction. On the other hand, these novel liquids system techniques will also remove the difficulties of using special facilities for hydrogen generation, their transportation, storage in traditional liquid phase hydrogenation industries.

Prof. Dumesic et al^[15—β1] in the University of Wisconsin reported that H₂ could be produced from oxygenated hydrocarbons by aqueous-phase reforming (APR) under mild conditions (423—530 K) over catalyst of Pt, Raney Ni or Raney-Ni modified with Sn. Another study on H₂ production from aqueous-phase reforming of ethylene glycol deduced the same results²². Aqueous-phase reforming of oxygenated hydrocarbons, such as methanol, for H₂ production takes place according to the following stoichiometric reaction:



These reactions may take place via formation of CO as an intermediate product, which is subsequently converted to CO₂ by water-gas-shift reaction. Generation of H₂ and CO₂ by aqueous-phase reforming at low temperature, however, is accompanied by selectivity challenges, since the reaction of H₂ with CO or CO₂ to form alkanes (C_nH_{2n+2}) is highly favourable at these low temperatures by methanation and Fischer- Tropsch reactions²³⁻²⁶

2.2 Comparison between methanol and the other hydrogen donor

In comparison with the catalytic transfer of hydrogen (CTH) using other primary aliphatic alcohols, such as isopropanol, as hydrogen donor, the use of methanol as hydrogen donor for the CTH has several advantages²⁷. Water is used as the promoter for the CTH using methanol as hydrogen donor. The CTH using methanol as hydrogen donor has a higher hydrogen atom utilization than the CTH using isopropanol as the donor. All hydrogen atoms in methanol molecule can be used for the reduction of unsaturated organics, but only 25% of hydrogen atoms in isopropanol molecular can be utilized. Additionally, hydrogen atom in a part of water can be utilized for the reduction of unsaturated organics, 2 mol hydrogen atoms in water can be utilized with the consumption of 1 mol methanol. Meanwhile, the CTH using methanol as hydrogen source in the presence of water also has higher hydrogen atom utilization.

Methanol vs. Ethanol and Propanol

The hydrogenation of phenol with hydrogen from the APR of methanol on the Raney Ni catalyst shows higher conversion than that on the Pd/Al₂O₃ catalyst. The following work (Figure 2.1) suggests superiority of ethanol over methanol²⁷.

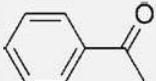
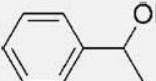
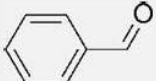
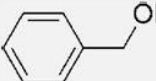
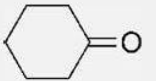
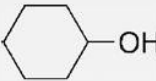
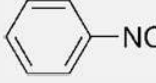
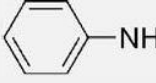
Substrates	Products	Alcohols	Water/Alcohols (mol/mol)	Yield (mol%)
		MeOH	0	2.56
		MeOH	0.5	12.88
		MeOH	0	5.07
		MeOH	0.5	20.12
		MeOH	0	1.31
		MeOH	0.5	5.07
		MeOH	0	4.65
		MeOH	0.5	51.45
		EtOH	0	5.10
		EtOH	0.5	12.50
		PrOH	0	6.66
		PrOH	0.5	14.43

Figure 2.1 Comparative studies of various alcohols as hydrogen source

2.3 Effect of water addition

Appropriate amounts of water in methanol could increase the conversions of styrene and nitrobenzene and/or selectivity of the desired products in the CTH using methanol as hydrogen donor highly. An Experimental result for the improved hydrogenation of styrene in presence of water is shown in the table 2.2.²⁷ Studies on other aromatic systems ex. Nitrobenzene show enhanced hydrogenation percentage in presence of water. As suggested by studies of mechanistic details with the help of deuterium tracer experiments it is suggested that the presence of water could improve the CTH using methanol as hydrogen donor through the fast conversion of formaldehyde into formic acid.

Table 2.2 Effect of water on CTH of styrene into ethyl benzene using methanol-water as hydrogen source

Entry	Water/methanol (mol/mol)	Styrene conversion (%)	Ethylbenzne selectivity (%)
1	0	26.3	100
2	0.1	74.4	100
3	0.25	100	100
4	0.5	100	100
5	1	100	97.6

2.4 Alkali promoted solvent system

Alkali promoted solvent system exhibit better yields for hydrogenation products thanunpromoted solvent systems. Further work is in progress in order to understand thereaction mechanism through detailed characterisation of the promoted samples. Theeffect of reaction temperature on phenol conversion is shown in Fig. 2.2. Both promoted (A) and unpromoted (B) palladium/alumina catalyst show a higher conversion at 473 K and thereafter decrease with increasing temperature²⁸.

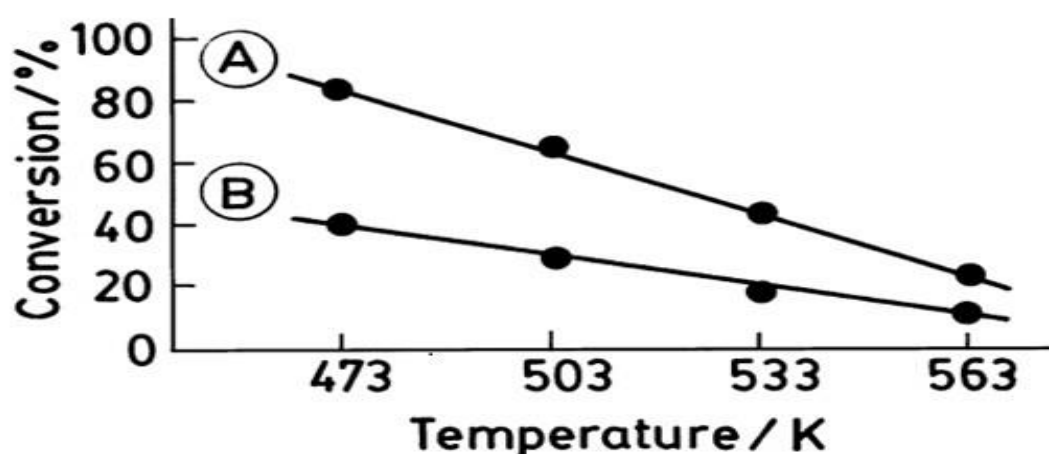


Figure 2.2 Comparison of (A) alkali promoted (B) alkali unpromoted phenol conversions using Pd/Al₂O₃ at various temperatures.

2.5 Temperature range

Variation of reaction temperature can affect catalyst activity and selectivity considerably. Various literatures are available for temperature studies of phenol hydrogenation reactions which suggest a reversible type relationship for conversion obtained versus temperature employed Fig 2.3 shows the influence of the reaction temperature on the activity of Pd/Al₂O₃. Similar results were obtained on the promoted samples and on Pd/MgO. As the temperature increases, the conversion reaches a maximum in the range 140-160°C and then decreases⁵.

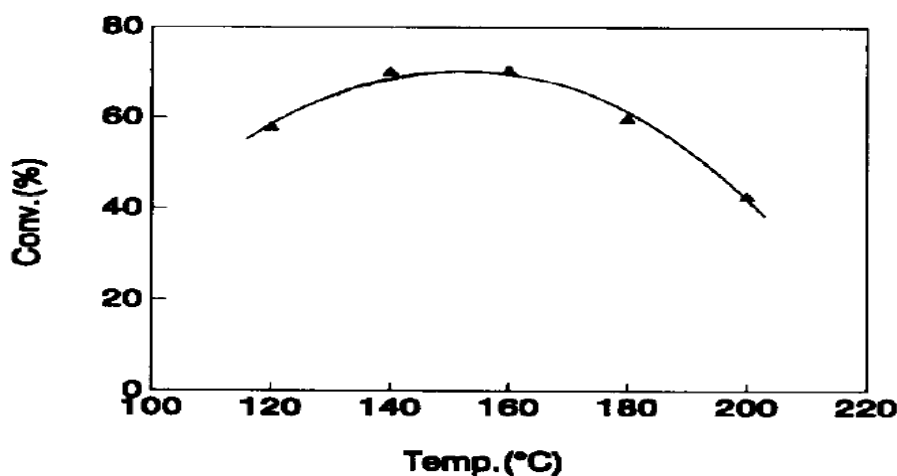


Figure 2.3 Relative phenol conversions at various temperatures over Pd/Al₂O₃

2.6 Catalyst screenings

Development of an efficient catalyst for phenol hydrogenation has attracted a great deal of attention in previous decade. Various catalyst screening studies have been performed aiming either for the higher conversion percentage or higher selectivity for a particular product. Several catalysts based on Ni, Co, Fe, Pt, Pd, and Ru dispersed on different supports have been studied for the HDO of phenol in the liquid or gas phase. There has been non-systematic study comparing the performance of various metals deposited over the same support. For example, Mortensen et al. studied the HDO of phenol in the liquid phase for Pt, Pd, and Ru supported on carbon. They reported the following order of activity for deoxygenation: Ru > Pd > Pt. Mortensen et al. Also investigated the performance of Ni supported on different materials (Ni/ZrO₂, Ni-V₂O₅/ZrO₂, Ni-V₂O₅/SiO₂, Ni/Al₂O₃, Ni/SiO₂, Ni/MgAl₂O₄, Ni/CeO₂-ZrO₂, Ni/CeO₂, Ni/C) for the HDO of phenol in the liquid phase. They found that Ni/ZrO₂ was

the most selective catalyst for the formation of cyclohexane.²⁹

It was suggested that phenol is adsorbed on coordinatively unsaturated metal sites in the oxide surface (Zr cations), stabilizing the phenoxide ion that interacts with Ni, facilitating the hydrogenation of the aromatic ring and producing cyclohexanone, which rapidly produces cyclohexanol. This alcohol would later be dehydrated to cyclohexene, followed by hydrogenation to cyclohexane.

Other metals such as Pd over other supports have been investigated too. Pd catalysts supported on SiO₂, Al₂O₃, and ZrO₂ were tested in the HDO reaction of phenol. The product distributions showed a remarkable dependence on the support used. Over Pd/SiO₂ and Pd/Al₂O₃ catalysts, the formation of cyclohexanone was favoured, whereas benzene was promoted over Pd/ZrO₂ catalyst. New catalysts such as Carbon Nitride and dual metal supported catalyst are emerging which give even higher conversion percentage for phenol hydrogenation.

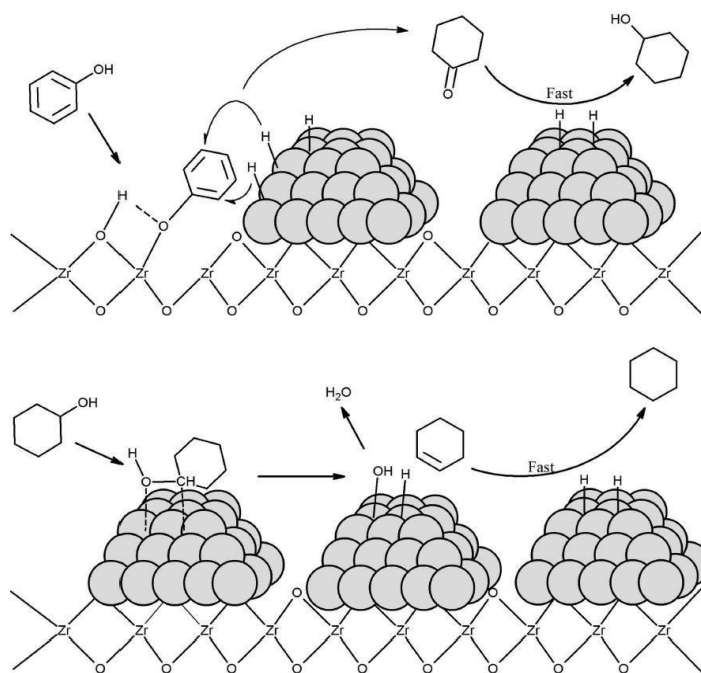


Fig. 2.4 Proposed reaction mechanism for HDO of phenol over an oxide supported nickel catalyst²⁹

However, our quest for a suitable catalyst is not very independent and based solely on the performance for phenol hydrogenation, but keeping the ultimate aim of the project which is

not only phenol hydrogenation but chemical conversion of phenolic monomers obtained from lignin depolymerisation we have to choose a catalyst which is efficient for depolymerisation reactions and also capable of hydrogenation. Ni supported Zeolite has been utilized for depolymerisation reactions as well as hydrogenation reactions.

Zeolite Solid Support If we heat a glass of water and we'll see steam rise off it sooner or later as it comes to the boil. You certainly don't expect the same thing to happen if you heat a rock—unless it's a special kind of rock called a zeolite, which traps water inside it. Zeolites are hydrated aluminosilicate minerals made from interlinked tetrahedra of alumina (AlO_4) and silica (SiO_4). In simpler words, they're solids with a relatively open, three-dimensional crystal structure built from the elements aluminum, oxygen, and silicon, with alkali or alkaline-Earth metals (such as sodium, potassium, and magnesium) plus water molecules trapped in the gaps between them.

Dual function catalysts consisting of metal and acid sites are usually used for transformation of bio-oil/bio-oil model compounds to high value hydrocarbons. Zeolites with optimum density and strength of acid sites seem to be suitable for hydrodeoxygenation of bio-oil/bio-oil model compounds. Metal and acid sites are generally involved in hydrogenation/hydrodeoxygenation and dehydration/hydrocracking/dealkylation/alkylation reaction mechanisms, respectively³⁰. HZSM-5 (30) with only weak acid sites showed lower cyclohexane selectivity compared with HZSM-5 (50) and HZSM-5 (80) which had both weak and strong acid sites³⁰ (where (30, 50, 80 represents Si/Al ratio)).

ACID Character of Zeolite The structural framework of zeolite includes the atoms of silicon and/or aluminium having tetrahedral coordination to four oxygen atoms. A zeolite consisting of only SiO_4 is electrically neutral but the presence of each AlO_4 in zeolite framework makes a negative charge which can be compensated by a cation³⁰⁻³¹. The presence of AlO_4 species and cations in zeolite structure changes catalytic properties of zeolites. By compensating the negative charges with protons, zeolites become strong solid acids³²

A detailed study for the Zeolite activity for different Si/Al ratios has been done²⁵. It suggests better hydrogenation activity for Metal supported HZSM-5 over metal alone. In phenol hydrogenation over the combined catalysts, Brønsted acid sites were mainly involved in dehydration of cyclohexanol to form cyclohexane as an oxygen-free product.

In our work, we are taking Ni-HZSM as catalyst which has been extensively studied

previously and a good background literature support is available for directions.

Ni Percentage Taking two different amounts of Ni impregnated zeolite surfaces and there studies for Hydrogenation and selectivity gives the following results⁵.

- In sample Ni-SiO₂-A, Ni wt% is 15.2%
- In sample Ni-SiO₂-B, Ni wt% - 20.3 %

The figure 2.5 suggests lower wt% imprigment for Ni over Zeolite surface for higher selectivity for cyclohexane. Moderate Ni wt% is favoured for complete hydrogenation product as reported by available litratures.

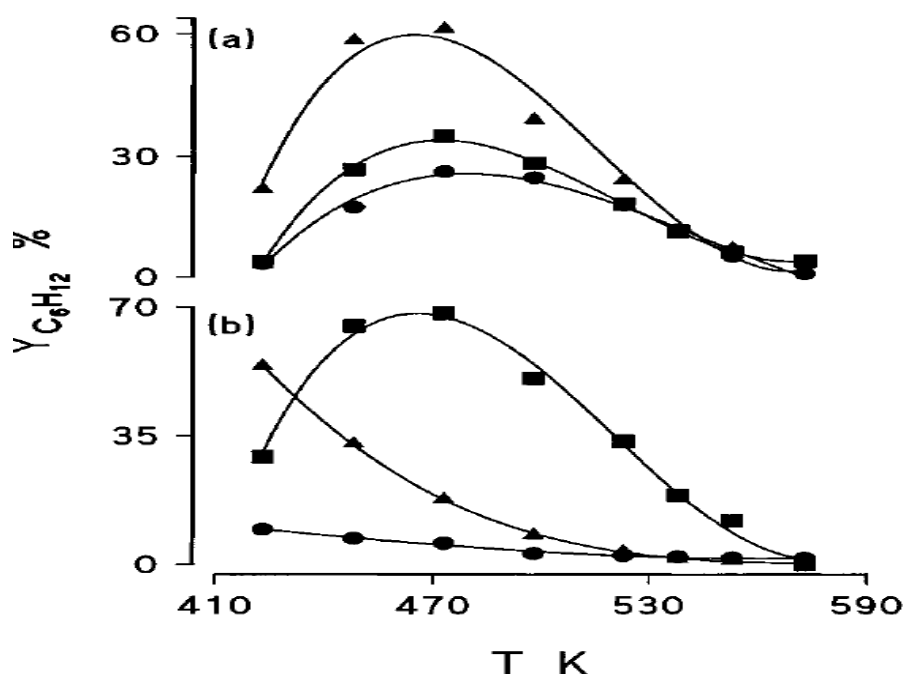


Figure 2.5 Cyclohexane⁵ yield as a function of temperature from a phenol (●), a cyclohexanone (■), and a cyclohexanol (▲) feed over (a) Ni/SiO₂-A and (b) Ni/SiO₂-B.

The most effective **Solvent System** for liquid phase hydrogenation is found to be methanol in presence of water. Mild alkaline water has been found to increase the phenol conversion. **Temperature** range has been found to affect the conversion percentage and maximum conversion has been found in 140°C-200°C. Above this temperature conversion falls again. **H-ZSM5** with Si/Al ratios above 30 has been found to increase the selectivity for cyclohexane and helps the dehydration of alcohols formed. Optimum **Metal (Ni)** loading (<20wt %) is found to enhance the conversion percentage and selectivity for cyclohexane.

3 CHAPTER 3: METHODS AND MATERIALS

3.1 Chemicals and apparatus used

Table 3.1 List of all the chemicals and apparatus used in this work

Sr.No.	Chemicals Used	Apparatus Used
1	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Beaker 500 ml , 100 ml
2	H_2SO_4	Volumetric flask
3	Tetradecane	Silica crucible
4	Nickel(II) nitrate hexahydrate	Hot air oven
5	Phenol	High temperature SiC Furnace
6	Methanol	High Pressure Reactor (PARR)
7	Dichloromethane	Conical flasks
8	Ethyl acetate	Heating mantle
9	NaOH	Pipettes
10	Gaseous N_2	Separating funnel
11	$\text{K}_2\text{Cr}_2\text{O}_7$	Test tubes
12	H-ZSM-5 catalyst	Magnetic stirrer
13	Tetrapropyleneammonium Bromide	pH meter
14	THF	GC-FID
15	Acetonitrile	Cyclohexane, Cyclohexene, Cyclohexanol
16	Chromatography grade Silica	Cyclohexanone (HPLC grade)
17	Sodium Aluminate	Vials
18	$(\text{NH}_4)_2\text{SO}_4$	
19	Chromic Acid	
20	H_2 gas	
21	Oxygen gas	
22	He gas	

3.2 Experimental Section

3.2.1 Catalyst preparation using different Al source

Beaker I :- 9gm (0.15 mol) chromatographic silica was dissolved in 2.5 N NaOH solution and stirred for 2-3 hr.

Beaker II :- 4.0gm of tetrapropylammonium bromide (TPABr) was taken as template source and was dissolved in 1.7ml of 96% H_2SO_4 diluted by using 50 ml of water.

Beaker III :- 1.35gm (0.0036 mol) $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as Al source dissolved in 25ml water. or

Beaker III :- 0.27gm (0.0036 mol) Sodium aluminate as Al source dissolved in 25ml water.

All the three solutions were mixed together and the gel formed is stirred for 20 minutes.

The pH of the solution was maintained at 11-12 and stirred further for 20 minutes.

The solution was transferred to polypropylene bottles and kept in oven at 95°C till 5 days for crystallisation. Crystals of TPA-ZSM-5 were obtained. Template removal is done by calcinations at a rate 10°C/min to 500°C and maintaining 500°C for 2 hours. Na-ZSM-5 thus obtained is ion exchanged with 0.1M (NH₄)₂SO₄ solution and again calcinations at 500°C for 3 hours and characterization was done by XRD, SEM-EDS, BET surface area calculations and acidity measurements techniques. The figure 3.1 represents whole synthesis scheme:-

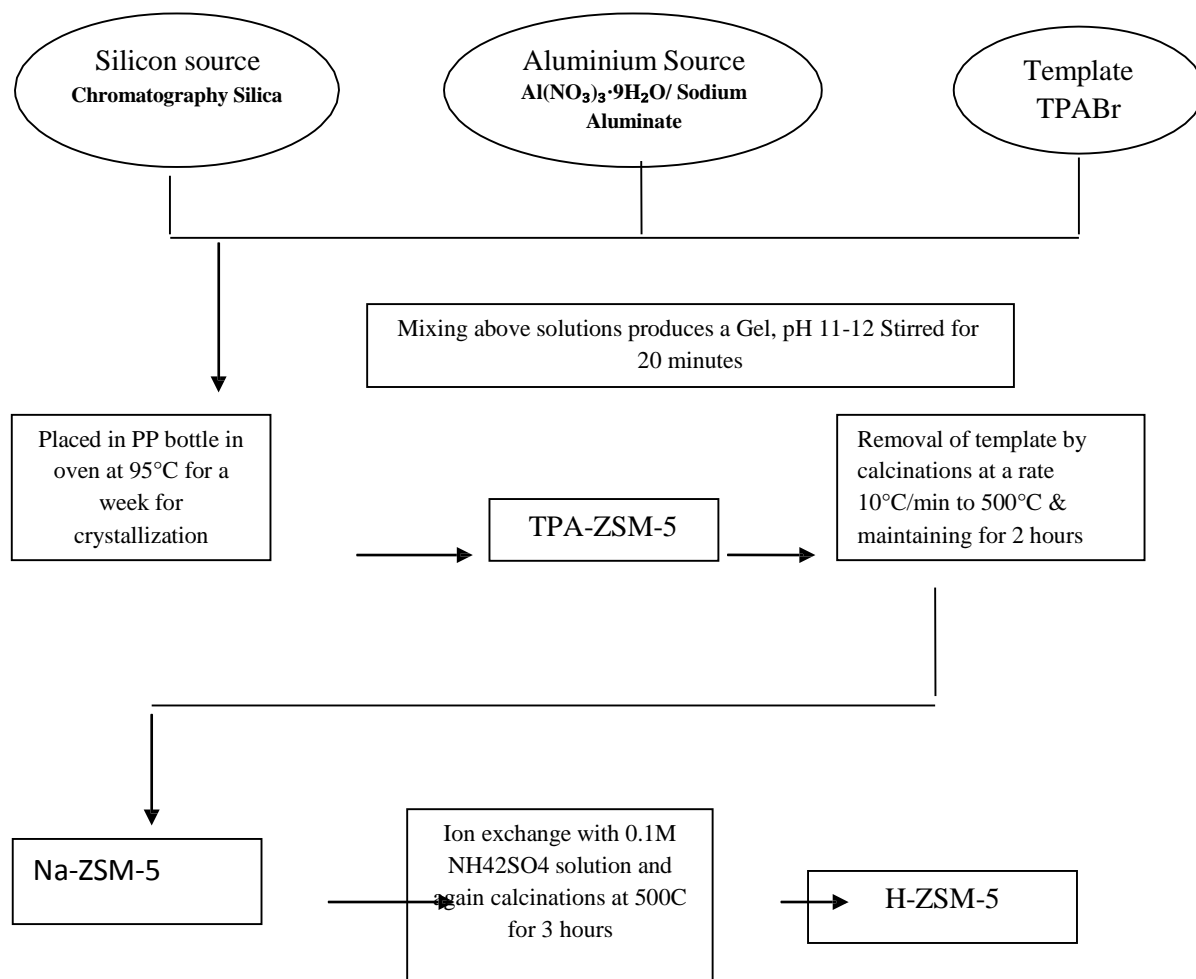


Figure 3.1 Synthesis scheme for catalyst preparation

Ni impregnation

5% Ni by weight of H-ZSM-5 was taken in the form of a solution of Nickel nitrate hexahydrate in water. Obtained HZSM-5 was stirred in the solution of Ni for 2 hours and then dried by evaporating water. Calcination of resultant was performed starting from room temperature at the rate of 50°C/min to 500°C and extended time for another 3 hours.

3.2.2 Phenol Treatment

6.5 ml of phenol along with 60 ml of solvent (methanol + water) was filled in the 100 ml vessel of batch reactor (PARR fig 3.2). Catalyst dose was taken 0.70gm i.e. 10% of phenol weight, temperature was varied from 60°C to 120°C, time for reaction was varied from 1 hours to 3 hours and solvent ratio of water/methanol was taken 1:1 ratio by volume. All these conditions were optimized for 10 reactions (table 3.2) to fix the highest conversion temperature and time.



Fig 3.2 Parr reactor with controller (4848)

Table 3.1 Predicted reaction conditions to be performed for highest conversion

S.NO.	Water (in ml)	Methanol (in ml)	Phenol (1:10 molar ratio of phenol to Methanol)	Catalyst (10 % of Phenol by Weight)	Temperature in(°C)	Time (hrs.)
1.	30	30	6.5	0.697894382	40°C	1hr
2.	30	30	6.5	0.697894382	60°C	1hr
3.	30	30	6.5	0.697894382	80°C	1hr
4.	30	30	6.5	0.697894382	100°C	1hr
5.	30	30	6.5	0.697894382	120°C	1hr
6.	30	30	6.5	0.697894382	40°C	3hr
7.	30	30	6.5	0.697894382	60°C	3hr
8.	30	30	6.5	0.697894382	80°C	3hr
9.	30	30	6.5	0.697894382	100°C	3hr
10.	30	30	6.5	0.697894382	120°C	3hr

All the above reactions were performed using batch reactor (Parr 4596) with continuous stirring with a propeller at 250-280 rpm throughout the experiment and the product obtained was filtered using Whitman filter paper and filtrate was acidified using dilute H₂SO₄ till pH reached 4-5. The volume of the product was made up to 100 ml using distilled water and 10 ml of the product was then extracted using 10 ml of Dichloromethane in separating funnel. Extraction was carried out three times ensuring the maximum organic content extract in organic phase and solutions were studied on GC-FID with further suitable dilutions.

3.3 Analytical section

3.3.1 Catalyst characterization

The structure of HZSM-5 was characterized by X-ray powder diffraction (XRD). The XRD patterns of samples were recorded on a analytical – X'Pert PRO through a 2θ range from 5° to 60° for HZSM-5 and 5° to 80° for Ni-ZSM-5 (step size 0.017, step

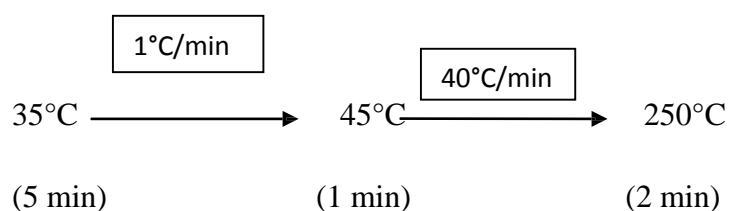
time 20 s) using CuK α radiation (1.54 \AA) at 40 kV and 100 mA. The surface morphology of the catalyst was studied by scanning electron microscopy on FEI Quanta 450 FEG apparatus equipped with Energy Dispersive Spectrometer (EDAX). Surface area, pore volume and average pore size were characterized and determined by N₂ adsorption–desorption (Micromeritics ASAP 2010).

3.3.2 Acidity analysis

The total acidity of the zeolite samples was measured using a potentiometric method of titration with n-butylamine.³³ n-Butylamine (0.1 N, 0.05 mL) was added to a dispersion of 0.15 g of zeolite sample in 90 mL of acetonitrile. This system was kept under steady stirring for 3 h. The suspension was then titrated using a base solution volume of 0.05 mL each time. The time elapsed before making a potential measurement was 2 min. The electrode potential variation (mV) was measured with a Toshcon CL46+ digital pH/mV meter. The total number of acidic sites per gram of catalyst was estimated from the total amount of base added to reach the plateau in the potential vs. milliequivalent (n-butylamine) per gram of catalyst curve, and the acid site density was calculated by considering the apparent surface area value of the corresponding zeolite sample.

3.3.3 Reaction Analysis

Organic mixtures obtained after extraction were diluted 50 times before injecting to GC-FID. Injector temperature for GC-FID was set at 280°C and detector temperature at 320°C. Tetradecane was used as internal standard (IS) and five standard concentrations of phenol and fixed concentration of tetradecane at 500 ppm were prepared for calibration. A two step program for GC-FID was employed which is



500 ppm of Tetradecane is used as internal standard for calibrating the response factor of phenol given by GC-FID. Various concentrations of phenol was prepared with constant concentration of IS in each solution and response factor (RF) of phenol and IS was monitored. Calibration curve was made and relative response factor (RRF)

was calculated which was used further in calculating the concentrations of phenol in reaction products. For calibration curves:-

Response factor for phenol
is

$$RF_{PhOH} = C_{PhOH} / A_{PhOH}$$

Response factor for
IS

$$RF_{IS} = C_{IS} / A_{IS}$$

Relative response factor

$$RRF = RF_{PhOH} / RF_{IS}$$

For unknown concentration of phenol:-

$$C_{PhOH} = (RRF \times A_{PhOH} \times C_{IS}) / A_{IS}^*$$

*Here RRF is the same as calculated from calibration curve.



Figure 3.3 Gas Chromatography coupled with FID

Same conc. of IS (500 ppm) was added to all the diluted reaction products and 1 μ l of this solution was investigated using GC-FID. Amount of converted phenol was calculated using back calculation.

4 CHAPTER 4: RESULTS AND DISCUSSION

4.1 Catalyst Characterization

Well characterized Ni-HZSM-5 catalyst was used for all phenol studies and characterization results obtained from the catalyst used in the experiment were as follows.

XRD diffractograms of synthesized zeolite catalyst **HZSM-5** and **Ni-ZSM-5** are shown in fig.4.1.

XRD diffractograms of synthesized zeolite catalyst **HAAS** and **Ni-AAS** are shown in fig.4.4.

The diffractogram of HZSM-5 confirmed when **Sodium aluminate** is taken as Aluminum source its typical MFI (Mordenite Framework Inverted) structure are verified. Average particle size of the synthesized zeolite HZSM-5 was calculated to be 11.78 μm . However, the SEM micrographs showed that the particles have nearly spherical morphology with particle size in the range of 2–8 μm . NiO phase was identified on the Ni-ZSM-5 catalyst from XRD diffractogram.

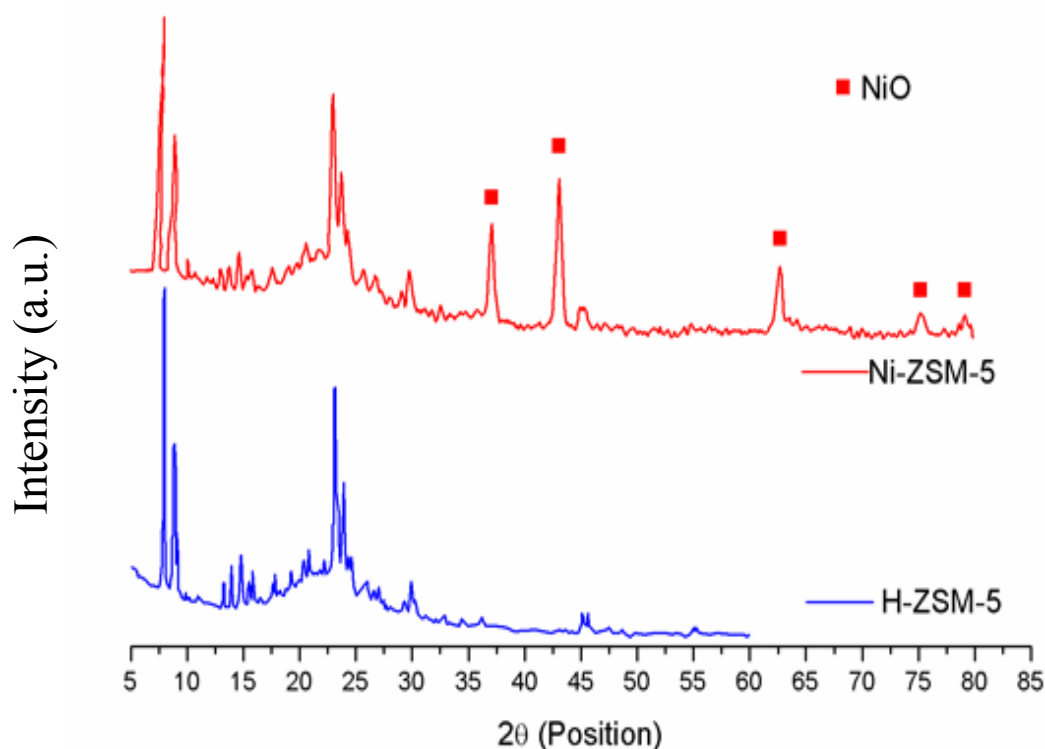


Fig: 4.1 XRD diffractogram of HZSM-5 and Ni-ZSM-5

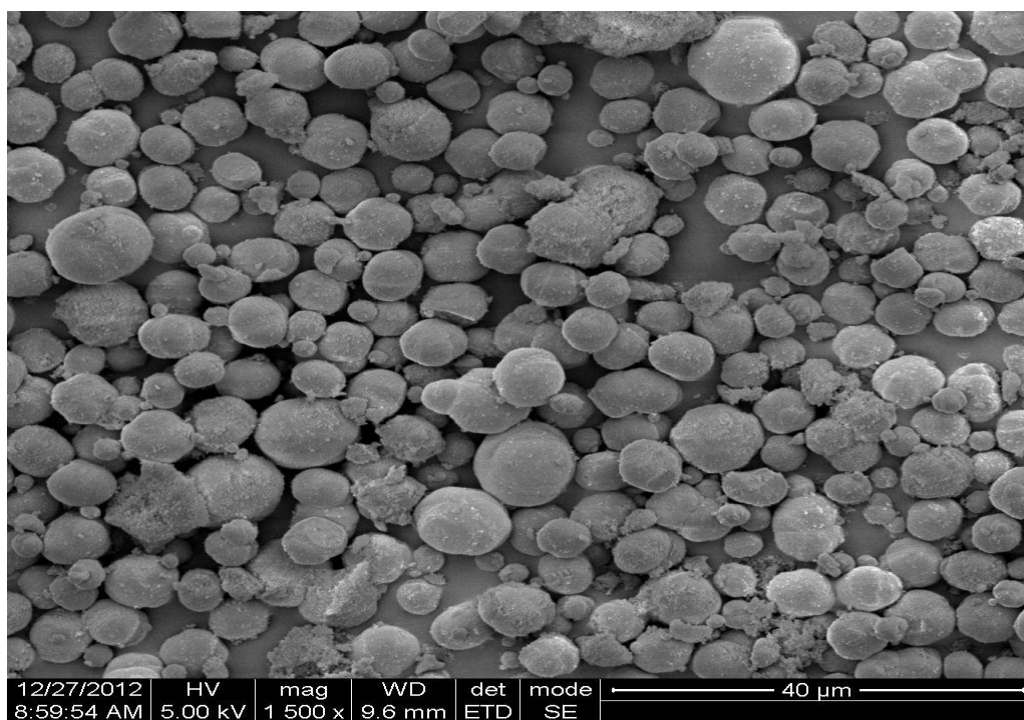


Fig: 4.2 SEM Image of H-ZSM-5

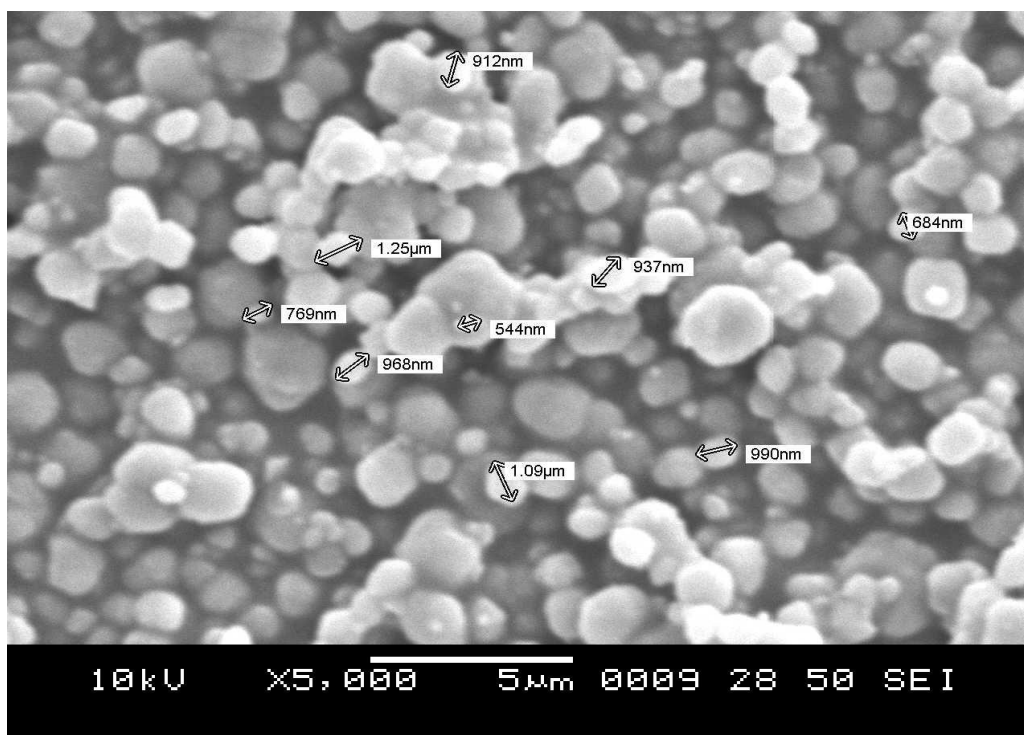


Fig: 4.3 SEM Image of Ni-ZSM-5

When $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is taken as Aluminum source the diffractogram of AAS(amorphous aluminosilicate) is obtained. XRD pattern shown in fig.4.4 shows that obtained pattern is for amorphous aluminosilicate has been confirmed from previous reported data. SEM micrographs showed that the particles have irregular morphology. NiO phase was identified on the Ni-AAS catalyst from XRD diffractogram.

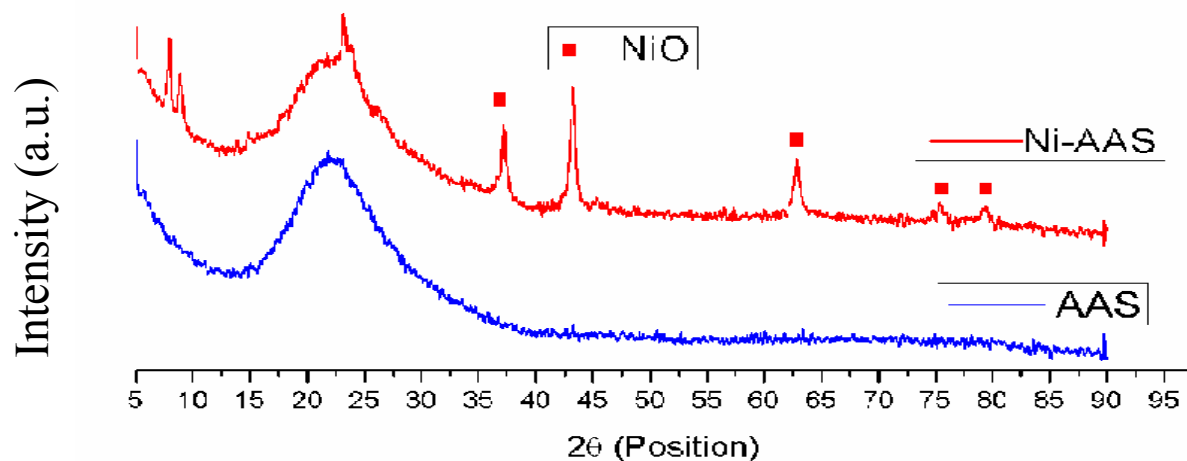


Fig: 4.4 XRD diffractogram of HAAS and Ni-AAS

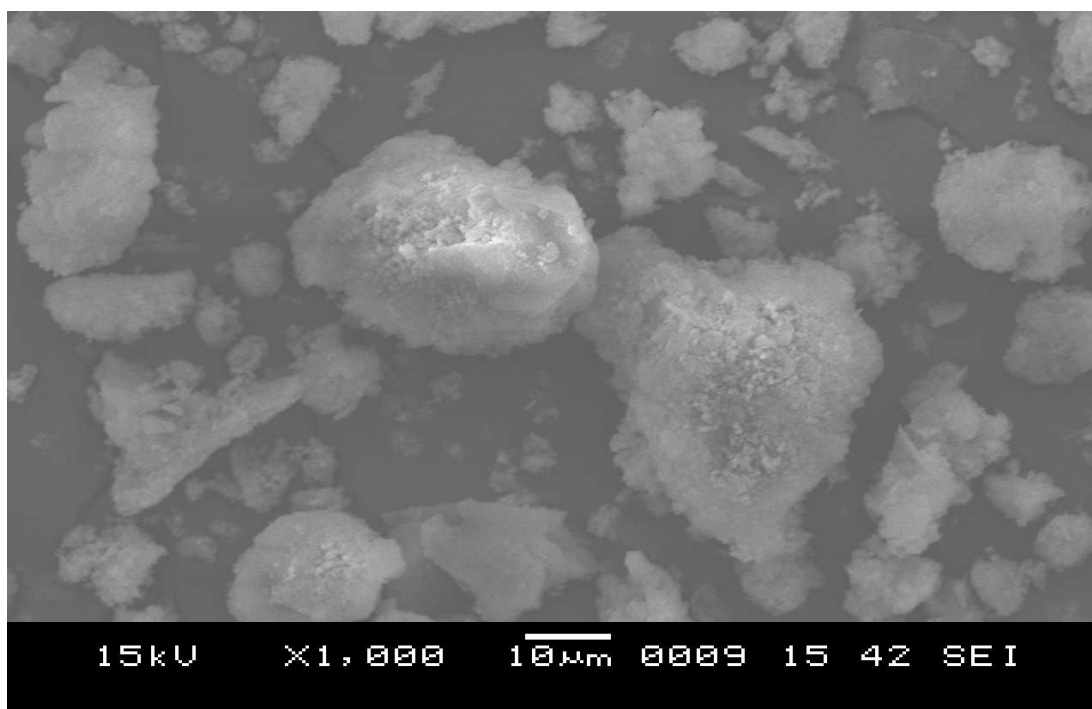


Fig: 4.5 SEM Image of H-AAS

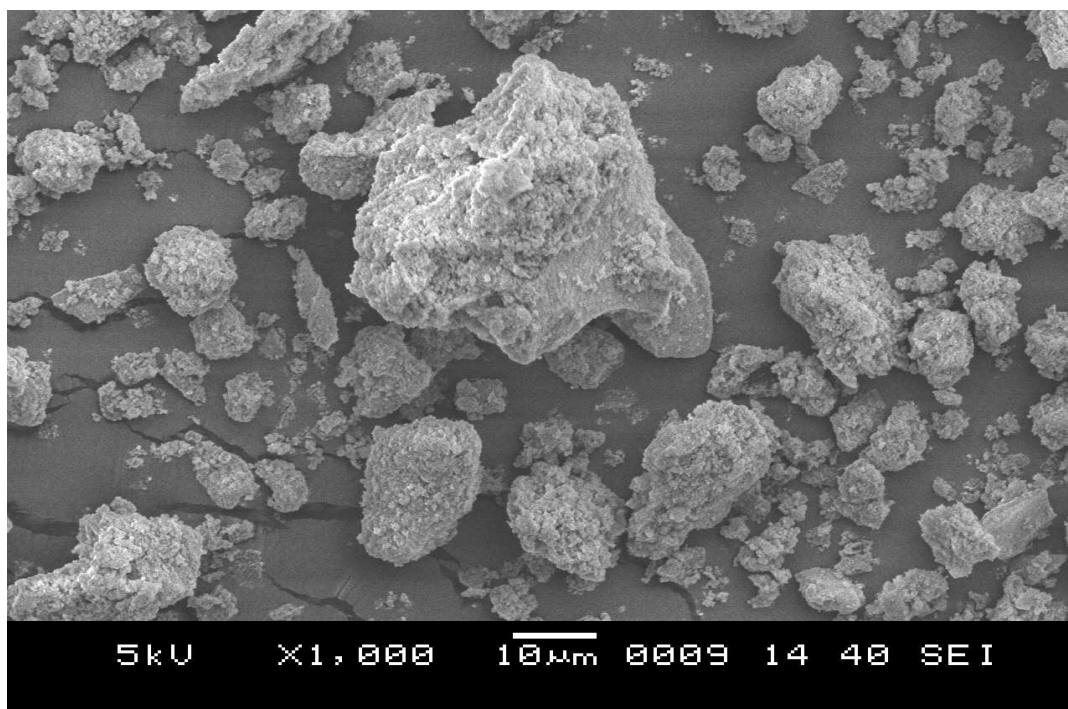


Fig: 4.6 SEM image of Ni-AAS

4.2 Acidity Analysis results

Milli equivalent of n-Butylamine/g of catalyst was plotted against milivolts (mV) and acidity of Ni-ZSM-5 is reported below in figure 4.7 - 4.8.

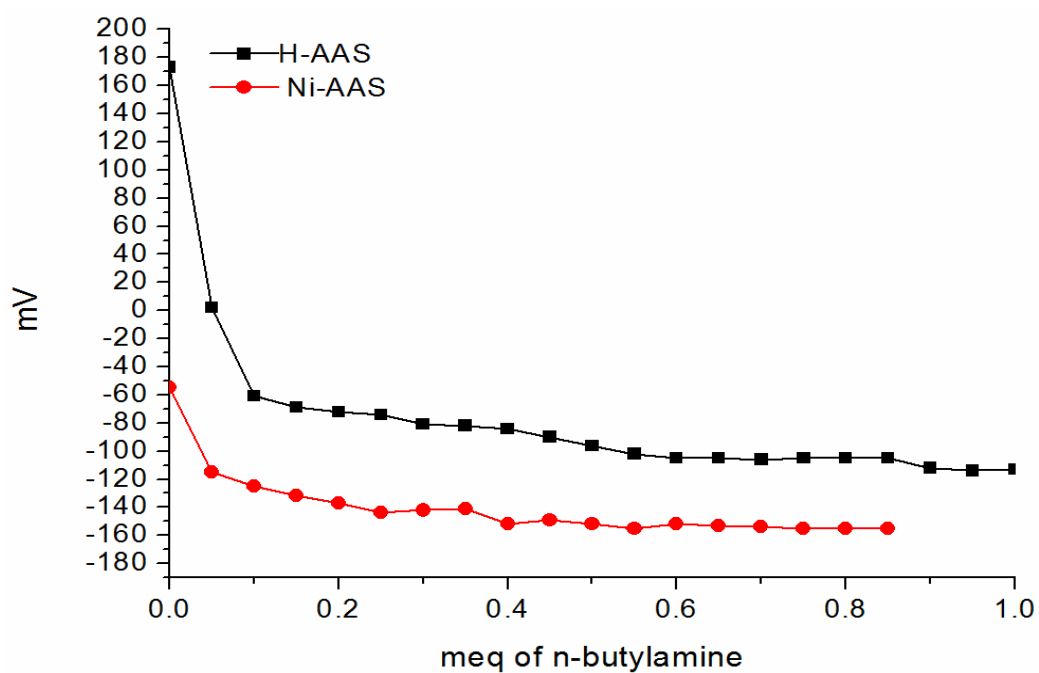


Fig. 4.7 Acidity analysis of HZSM-5 and Ni-ZSM-5

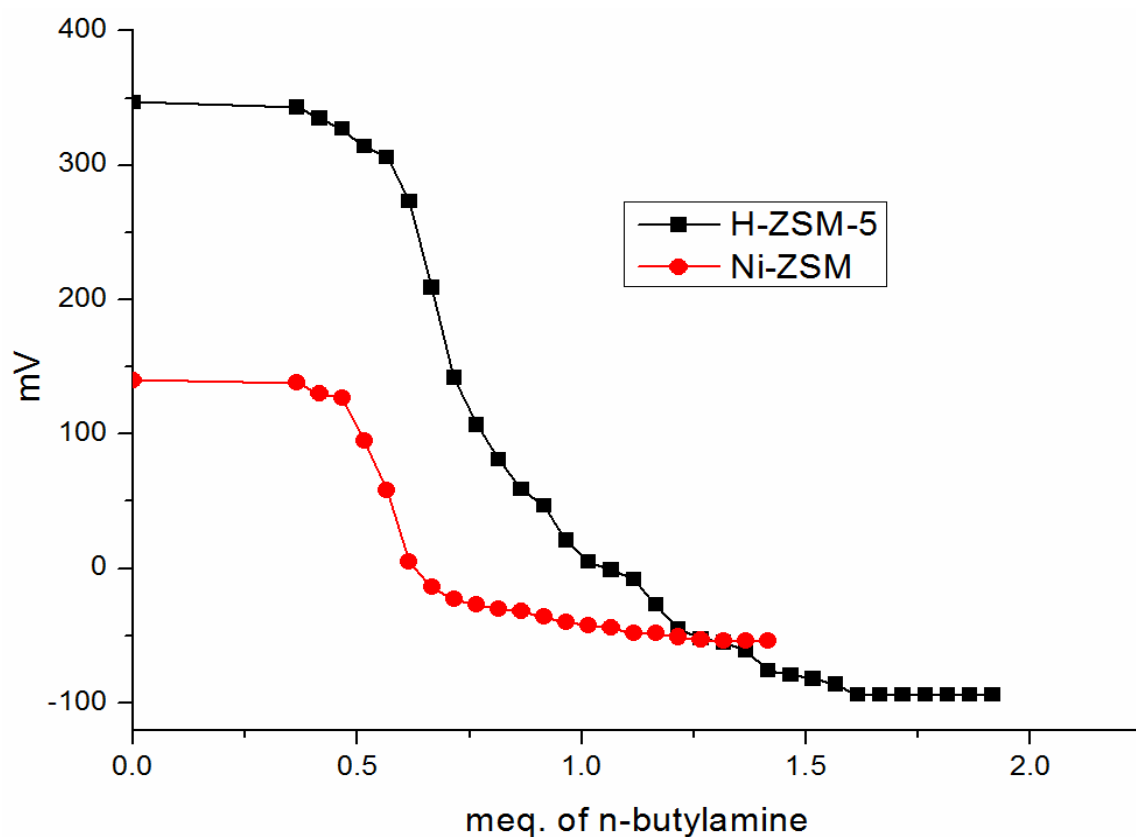


Fig. 4.8 Acidity analysis of HZSM-5 and Ni-ZSM-5

Interpretation from graph

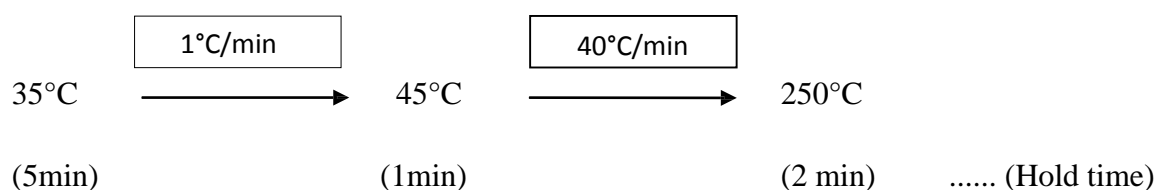
Table 4.1 summarizes the nature of acidic sites in H-AAS, Ni-AAS, H-ZSM-5 and Ni-ZSM-5 obtained from graph and the total acidity sites of synthesized catalyst is reported.

Table 4.1 Summary of the acidic sites and surface area calculated from BET

Nature of acidity of sites	Mv	H-AAS (milli eq/g)	Ni-AAS (milli eq/g)	H-ZSM-5 (milli eq/g)	Ni-ZSM-5 (milli eq/g)
Very strong(vs)	>100	0.11	Nil.	5.3	3.38
Strong(s)	0-100	0.13	Nil.	1.86	0.73
Weak(w)	0-(-100)	3.06	0.13	3.93	Nil.
Very weak(vw)	<-100	3	5.46	1.73	Nil.
	Total acidic sites	6.3(v s)	5.59(s)	12.82	4.01
BET surface area (m² g⁻¹)		350.2	265.23	386.43	315.95

4.3 Reaction analysis -GC-FID analysis

Organic mixture obtained after extraction were diluted 50 times using DCM before injected to GC-FID. Injector temperature for GC-FID was set at 280°C and detector temperature at 320°C. Tetradecane was used as internal standard and five standard concentrations of phenol and fixed concentration of Tetradecane at 500 ppm was prepared for calibration. A two step program for GC-FID was employed which is



Calibration curve obtained for five standard concentrations of phenol has been shown in figure 4.5 which gave 97% linear fitting. Graph is plotted for ratios of response factors for phenol and internal standard versus concentration ratio of both. Slope of the curve gives relative response factor (RRF) which was further used in calculating the concentration of left phenol in reaction mixture obtained after reaction.

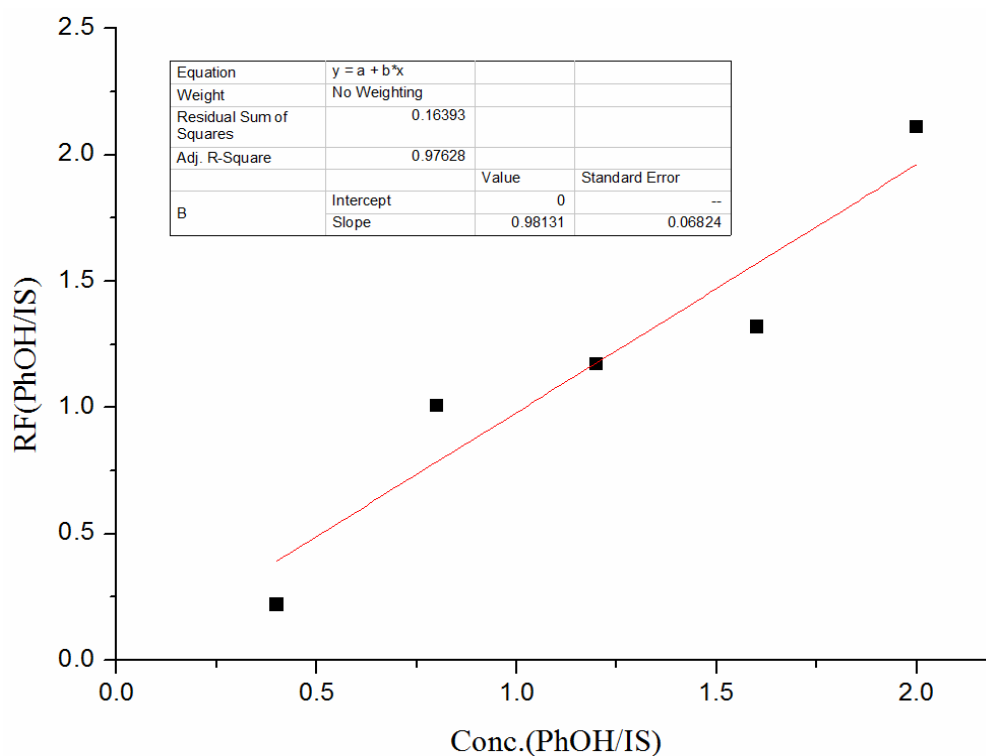


Fig 4.9 Calibration curve for phenol

Hydrogenation of phenol in methanol-water solvent was carried out in a 100 mL stainless steel autoclave. Appropriate amount of phenol, methanol-water and Ni-ZSM-5 catalyst were added into the reactor together. The reactor system was then purged with N₂ three times subsequently, the autoclave was heated up to the required temperature. During the experiment, the stirring rate was fixed at 250 rpm. The products were separated from water by phase separation technique: firstly, the catalysts were removed from the liquid by filtration, the obtained liquid phase was then transferred to a separatory funnel, the aqueous phase was collected for circulation. The organic phase was collected and analysed by an instrument of Agilent-6890-GC-5973-MS equipped with 30mHP-5 capillary (5% phenyl methyl polysiloxane).

The experimental results of solvent (methanol-water) for phenol hydrogenation over NiZSM5 catalyst are summarized in Table 4.2. Hydrogenation of phenol at 67 °C for 1 h obtains the phenol conversion degree of 93%. The organic phase (products) and aqueous phase (solvent) were separated *via* phase separation technique using Dichlormethane.

Table 4.2 Experimental results of Phenol conversions at different time and temperature

S. No.	Temp °C	Time	Phenol AR	AR (IS)	Conc. in ppm	Unreacted Conc. of original phenol conc. in (ppm)	% Phenol Conversion
1	40	1hr.	868636	3301903	134	18899	73
2	60	1hr.	897465	4272691	107	15090	78
3	67	1hr.	204588	3301584	31	4451	93
4	80	1hr.	731978	3596278	103	14622	79
5	100	1hr.	1271664	4354836	148	20979	70
6	120	1hr.	1223278	3651567	170	24067	65
7	40	3hrs	939225	3515294	136	19195	72
8	60	3hrs	560732	2310866	123	17432	75
9	67	3hrs	353441	3247887	55	7818	88
10	80	3hrs	971633	3388529	146	20600	70
11	100	3hrs	1049725	3100585	172	24323	65
12	120	3hrs	820994	2329148	179	25323	63

AR-Area; Conc.-Concentration; IS-Internal Standard

As the temperature and time increases % conversion of phenol reduced. Maximum % phenol conversion is 93%, almost 100% at 67 °C in 1hour but no reduced product is seen in GC analysis. It may be due to three factors

- 1) gasification of products
- 2) solubility of phenol degraded compounds in aqueous phase
- 3) Solvent extraction from aqueous phase system

Conversion percentage obtained experimentally for above 12 reactions by varying time and temperatures parameters at fix solvent ratio and catalyst dose is representing graphically in fig. 4.10 shows that as the temperature and time increases % conversion of phenol reduced.

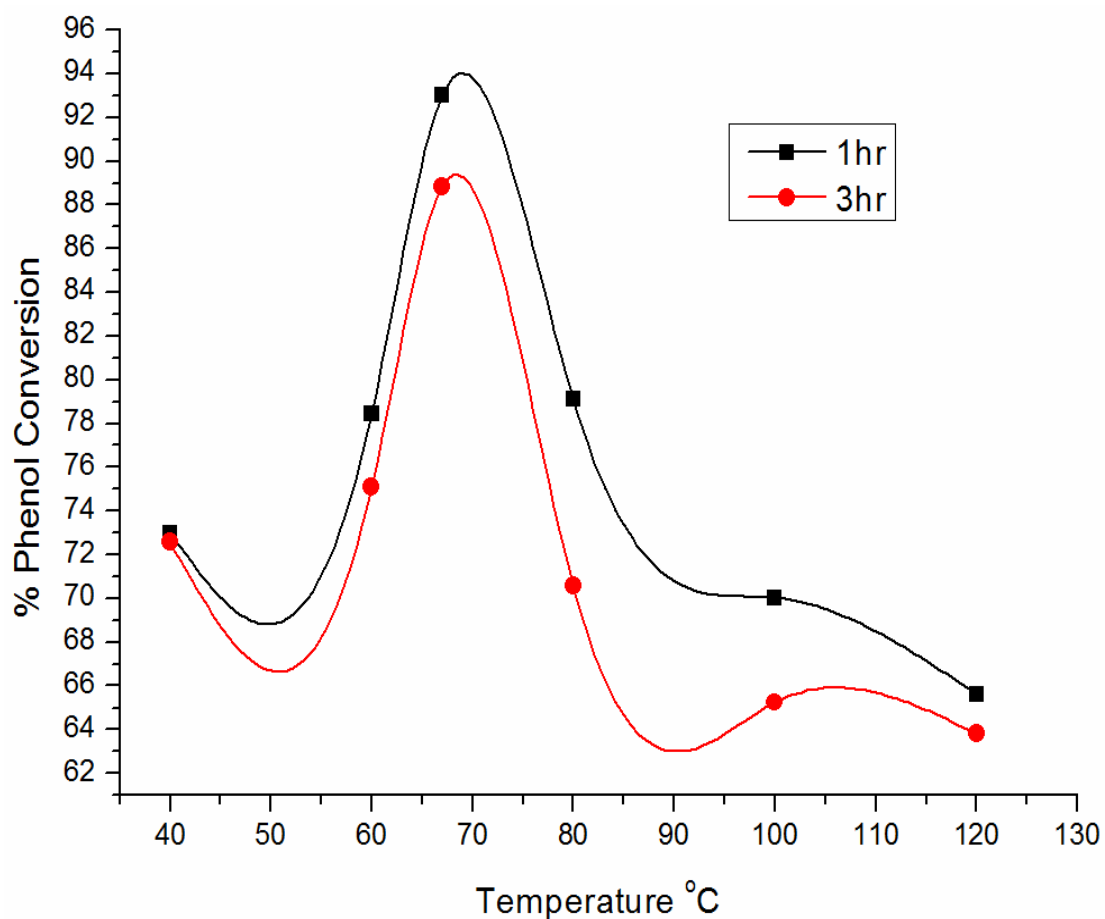


Fig. 4.10 Experimentally obtained conversion percentage of phenol at lower temperature region.

4.4 GC Chromatogram

This is the chromatogram obtained from a standard samples mixture of 500 ppm cyclohexane, cyclohexene, cyclohexanol, cyclohexanone and phenol. the largest peak in the chromatogram is the DCM solvent peak (= ~99.99 %) and that the other peaks, relative to the solvent peak, are extremely small and cannot be observed in this spectrum.

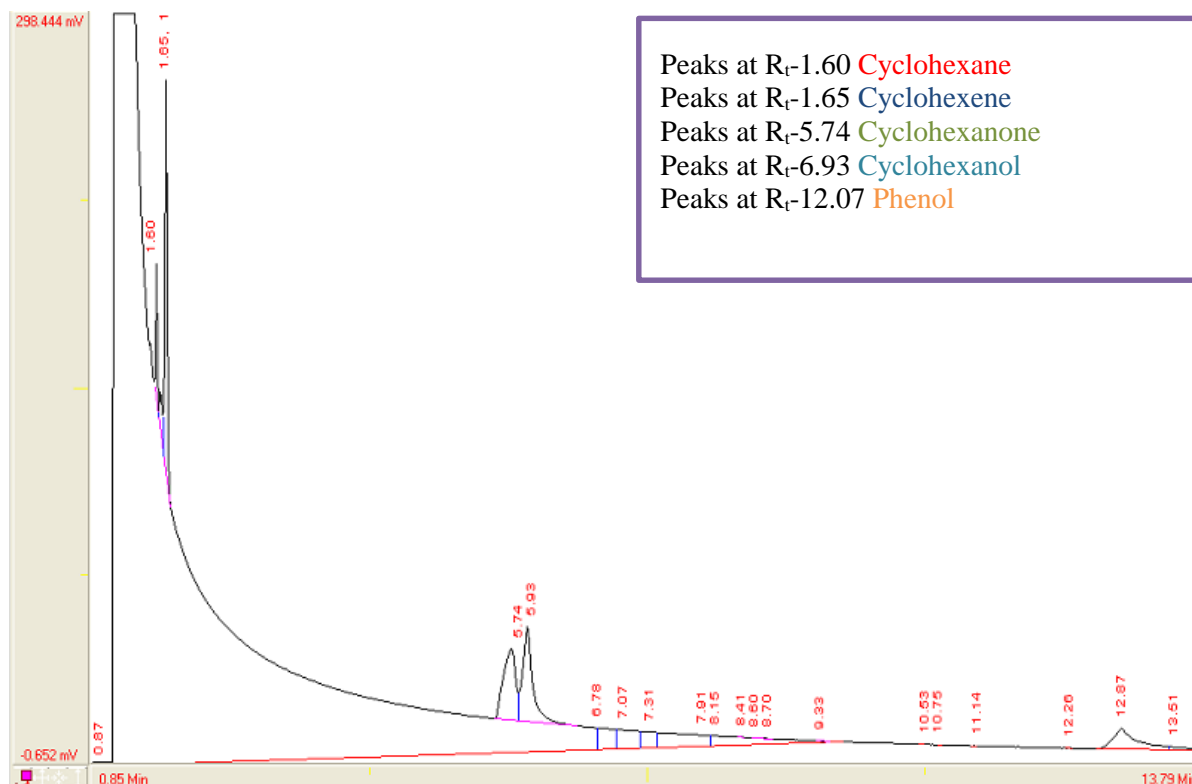


Fig 4.11 chromatogram obtained from a standard samples mixture

CHAPTER 5: CONCLUSION AND FUTURE SCOPE

Conclusions

- The efficiency of the H-ZSM-5 zeolites as catalysts is related to their morphological and particular properties as well-defined crystalline structure, high internal surface areas, uniform pores and good thermal stability.
- H-ZSM-5 has been synthesized with two different precursors of Al source as it shows a great effect on ZSM-5 crystallization which leads to change in the properties of the final product like crystallinity, morphology, surface area and no. of acidic sites present in ZSM-5 zeolite which further leads to change its catalytic activity.
- Sodium aluminate as Al source gives spherically shaped particles while with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as Al source, irregular shape of particle has been obtained.
- Results shows that average particle size increased when aluminum nitrate is used as Aluminum sources in comparison to sodium aluminate, whereas surface area increased with sodium aluminate as Aluminum sources in comparison to aluminum nitrate as Al source.
- Number of acidic sites present in the catalyst having very high importance insitu aqueous phase reforming hydrogenation reactions to generate more hydrogen.
- In our case sodium aluminate as aluminum source has very high number of acidic sites in comparison to aluminum nitrate as aluminum source.
- Ni-ZSM-5 has been found as an effective catalyst for aqueous phase phenol hydrogenation 10% catalyst dose by weight with respect to phenol taken gives almost 93% conversion of phenol; product selectivity is still a quest.
- Temperature and time of reaction has a marked effect in phenol conversion. Reaction has highest conversions at temperature near 67°C to 70°C . Increasing temperature results in lower phenol conversion for the reaction. Maximum 93% phenol conversion is reached at time 1hr with 10 % catalyst dose. Further increase in time resulted in reduced phenol conversions.
- Reduced products like cyclohexane, cyclohexanol or cyclohexene are obtained from this kind of system.

Future prospects

Qualitative and quantitative study of products obtained can give an insight for reaction mechanism and kinetics of individual steps during the reaction. Selectivity of the products will result in development of useful chemicals by successful employment of this process on large scales. RSM model used will be very effective for this kind of systems and we can rely on the model for predicting the outcome before investing in the process and it also predicts the higher yields at even lower temperatures which can be explored minimizing the input. Mechanistic studies will also help in modification of catalyst Ni-HZSM-5, doping with suitable promoters and lowering the energy which we are putting into the reaction.

Finally we can use this study as the basis for the processing of higher substituted phenols, the kind we get in lignin depolymerisation and successful processing of those will lead to higher hydrocarbon content which in turn can be used as added fuels.

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