LIQUID PHASE CATALYTIC HYDROGENATION OF PHENOL

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Computer Aided Process Plant Design)

By

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CANDIDATES DECLERATION

I hereby declare that the work, which is being presented in this dissertation entitled "**LIQUID PHASE CATALYTIC HYDROGENATION OF PHENOL**" for the partial fulfillment of the requirements of the award of the degree of **Master of Technology** in **Chemical Engineering** with specialization in Computer Aided Process Plant Design(CAPPD),and submitted in the **Department of Chemical Engineering** of **Indian Institute of Technology Roorkee,** Roorkee, is an authentic record of my own work carried out during the period from June 2004 to June 2005 at Indian Institute of Petroleum, Dehradun, under supervision of Dr. M.P.Saxena, Scientist, Indian Institute of Petroleum, Dehradun, Dr.S.C.Gupta, Professor, Indian Institute of Technology Roorkee and Dr.V.K.Agrawal, Associative Professor, Indian Institute of Technology Roorkee, Roorkee.

The matter, embodied in this dissertation has not been submitted by me for the award of any other degree.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ABSTRACT

Liquid phase hydrogenation of phenol to cyclohexanone was investigated over commercial carbon supported palladium catalyst. Study was to find the effect of temperature, catalyst load and metal content on the selectivity and phenol consumption rate. Experimental study was carried out in a slurry phase, isothermal batch process, using an autoclave. The major products of the hydrogenation reaction were cyclohexanone and cyclohexanol. The selectivity for cyclohexanone was up to 98%, with complete conversion of phenol depending on the temperature, catalyst weight and metal content. Phenol consumption rates increased with the temperature and catalyst load. Decrease in metal content reduced the phenol consumption rate, while selectivity was not much affected. Apparent activation energy for the phenol conversion was found to be 31.51 kJ/mol.

NOMENCLATURE

r_{ph}	reaction rate with respect to phenol	mole/lit-min
r_{H2}	reaction rate with respect to Hydrogen	mole/lit-min
r_{one}	reaction rate with respect to cyclohexanone	mole/lit-min
r_{nol}	reaction rate with respect to cyclohexanol	mole/lit-min
S	selectivity	
C_{ph}	concentration of phenol	mole/lit
C_{nol}	concentration of cyclohexanol	mole/lit
C_{none}	concentration of Cyclohexanone	mole/lit
P_{h2}	partial pressure of hydrogen	atm
C_{pd}	palladium content in catalyst	
T	Temperature	^{0}C
t	Time	min
ρ	Density	kg/lit

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CHAPTER 1

INTRODUCTION

1. GENERAL

Universe comprises of large to tiny particles which are formed by either physical or chemical reactions. Physical reactions involve breaking of large molecules into smaller particles, whereas in the case of chemical reactions, the transformation from one state into another state occurs. The chemical reactions are great concern to deal with. It depends on many factors such as temperature, pressure, concentration and contact time. The mankind is trying to control over the chemical reactions. There are many ways of classifying chemical reactions. In chemical reaction, probably the most useful scheme is the break down according to the number and types of phases involved, the big division being between the homogenous and heterogeneous systems. A reaction is homogeneous if it takes place in one phase alone. A reaction is heterogeneous if it requires the presence of at least two phases to proceed at the rate that it does. It is immaterial whether the reaction takes place in one, two, or more phases ; at an interface ; or whether the reactants and products are distributed among the phases or are all contained within a single phase. All that counts in that at least two phases are necessary for the reaction to proceed as it does. The chemical reactions are also classified based on the temperature requirements as (i) exothermic reactions and (ii) endothermic reactions. The exothermic reactions liberate energy during the reaction while endothermic reactions consume energy.

1.1. CATALYST

A catalyst accelerates the rate of a chemical reaction, but does not undergo any permanent change. Reactants (or just one reactant) adsorb on to active sites and are converted to products at a lower temperature and more quickly than those would convert in the absence of a catalyst.

A catalyst lowers the energy barrier or activation energy in the transformation of reactants to products, which increases the net rate of reaction. The difference between the energy states of the reactants and products may be endothermic or exothermic heat of reaction based on type of reaction take place. It is of great importance to recognize that both the net enthalpy and net free energy are unaffected by the presence of the catalyst. A catalyst enhances the kinetics of reaching equilibrium. Thus the reaction enthalpy ΔH and reaction free energy ΔG (and consequently, the equilibrium constant K) are not altered by the presence of a catalyst. The rate of reaction is inversely proportional to the activation energy. The activation energy is measure of the slowest step for the entire process of converting reactants to products. The catalyst directs the reactants to desirable products, i.e, selectivity, by preferentially lowering the activation energy for a particular step in the reaction sequence, and increases the rate at which this step proceeds.

An analysis of the chemical equilibrium composition in systems of organic reactants normally indicates that a large number of reactions possible. However, in most cases, only one or limited number of products are desired. Most of the potential by-products have a detrimental effect on the feasibility and operation of a particular process. Selectivity determines the yield of the desired product as well as the yield of waste that has to be disposed. Both yields have a significant effect on the economics of processes.

Environmental regulations are a major driving force for improving selectivity. Therefore, the selectivity is a key factor in the evaluation of chemical organic processes. Catalysts are a determining factor in the kinetics of chemical reactions, thus affecting the selectivity of chemical processes directly.

Though many developments have taken place in the catalyst preparation and study, the exact role of the catalyst is still unknown. Different catalysts have to be studied experimentally for their effect on different reactions of the compounds, to find the best catalyst.

In catalytic reactions itself, the reactions are classified as homogeneous and heterogeneous catalytic reactions. In the homogeneous catalytic reactions, the reactants, products, and the catalyst used will be in the same phase. But in heterogeneous, the reactants, products, and the catalyst either one of them will be in different phase. The heterogeneous catalytic reactions are great concern to deal and getting familiar in the field of reaction engineering, and in most of the chemical industries are involving with part of reactions In this study the heterogeneous type of catalytic reaction was taken. In the case of heterogeneous catalytic reactions, factors effecting the selectivity and rate are many fold. The complexity in the heterogeneous catalysis increases as, both activity and selectivity are sensitive to changes in catalyst structural properties where, metal loading, surface acidity/basicity, and the inclusion of promoters (alkali metals, alkaline earth metals, and lanthanide), have all been found to impact on catalyst performance.

1.2. CATALYTIC HYDROGENATION

Hydrogenation is a chemical reaction in which unsaturated bonds between carbon atoms are reduced by attachment of a hydrogen atom to each carbon. The process thus results in the saturation of the carbon atoms, meaning that each carbon atom has 4 other atoms attached to it. Numerous important applications are found in the pharmaceutical and petrochemical industries. The unsaturated compounds are partially hydrogenated, providing an increase in stability.

Hydrogenation typically uses hydrogen gas as a reactant and an undissolved (or "heterogeneous") metal catalyst, such as nickel, palladium or platinum.

Catalytic hydrogenation of organic compounds, an important tool in organic synthesis, developed from Sabatier's(1902) discovery of the ability of metal catalysts to activate hydrogenation of double and triple bond in the vapor phase at atmospheric pressure. This led to researchers to investigate on many other metals for the similar activity. For example, Catalytic hydrogenations of alkenes produce the corresponding alkanes. The reaction is carried out under pressure in the presence of a metallic catalyst. Common industrial catalysts are based on platinum, nickel or palladium, for laboratory synthesis.

In catalytic hydrogenation process certain metals in finely divided form or dispersed on carriers induce reaction to take place on their surface. That is a reducible function or ring system of an organic compound may be converted to the desired state by subjecting it, in solution or suspension in a suitable medium, to attack by hydrogen under suitable pressure and pressure in the presence of a prescribed amount of a finely divided metal or such a metal on a support.

Generally Group-VIII metals are found to have good behavior as hydrogenation catalysts when supported on highly porous materials such as alumina. The activity and selectivity of these catalysts are strongly dependent on the type of support, the method of catalyst preparation, the activation conditions, and the operational conditions that is the pressure and temperature at which the reaction is carried out.

1.3. VAPOR PHASE AND LIQUID PHASE HYDROGENATIONS

Catalytic hydrogenation processes are being used in the chemical industry as a means to obtain many useful products and intermediates. As hydrogen is always in the gas phase, it is said that there is a vapor-phase or liquid-phase hydrogenation on the state in which the other reactants are fed.

1.4. PRODUCTION OF CYCLOHEXANONE

Cyclohexanone is a key raw material in the production of caprolactum for Nylon 6, and adipic acid for nylon 66, with greater than 90 percent of world production. Caprolactum capacity (about 3MT/annum) based on the cyclohexanone oxidation route. Cyclohexanone is produced catalytically by either air oxidation of cyclohexane or hydrogenation of phenol. Hydrogenation of the phenol was started as early as in 1913. Hydrogenation of phenol is a complex reaction with many reaction possibilities.

1.4.1. Merits of Hydrogenation Route

Phenol is an established environmental toxin arising from a variety of industrial sources associated with petrochemicals and polymer manufacture. A catalytic hydrogen treatment of such waste to generate reusable raw material is certainly preferable to the standard destructive route by incineration. A move from incineration to hydrogen treatment represents immediate savings in terms of fuel and/or chemical recovery.

Technology based on cyclohexane oxidation accounts for 80 percent of the nominal world capacity of pure cyclohexanone. But cyclohexanone oxidation involves high temperature and pressure, and large quantities of flammable materials. In addition the process generates large amounts of further oxidation products which lower yield and complicate the recovery, and purification stages. The overall process yields, with respect to benzene, are always lower than 90 percent and typically in the range 75-85 percent.

In the hydrogenation route phenol is produced from cumene together with acetone as a by product. The organic yields are in the range of 90-95 percent with respect to benzene. In turn cyclohexanone can be obtained from phenol either in one step partial hydrogenation to cyclohexanone or two steps, complete hydrogenation to cyclohexanol and dehydrogenation to cyclohexanone. One step partial hydrogenation of phenol, can kept lower benzene consumption than in the cyclohexane oxidation route. Fig.1.1 shows the two routes of production of cyclohexanone.

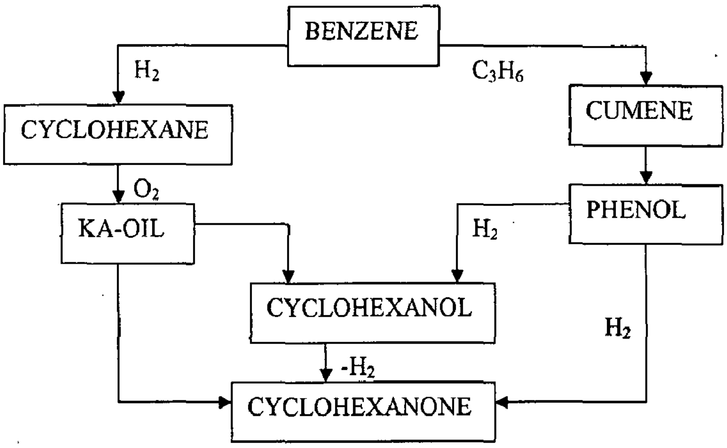

Fig.1.1. Cyclohexane production routes

1.5. RECENT DEVELOPMENTS

An overview of the recent literature on selective catalytic hydrogenation reveals, if not an avalanche, certainly a proliferation of papers that describe the selective hydrogenation of phenol to cyclohexanone in the vapor phase.

The hydrogenation of phenol in vapor phase has been reported for a range of palladium, platinum and nickel based catalysts. Reaction selectivity, in terms of cyclohexanone production, is strongly dependent on reaction conditions and under a narrow range of conditions; selectivities in excess of 95% have been quoted in the literature of vapor phase hydrogenation. Though liquid phase hydrogenation of phenol was started long before, a scant literature is available for the liquid phase hydrogenation of the phenol.

1.6. PROSPECTIVES OF LIQUID PHASE HYDROGENATION

Though many of the industrial hydrogenation processes are now being carried out in the vapor phase, there are some disadvantages in carrying out vapor phase hydrogenation. Disadvantages of vapor phase hydrogenation are high-energy consumption, devices cost and deactivation of the catalysts caused by coking during the reaction due to high temperatures employed.

In general, temperature gradients arising from the heat transfer limitations are not as prevalent under liquid phase reaction conditions compared to the vapor phase, because of the high heat capacities and thermal conductivities of liquid phase when compared with gas phase. Thus carrying out hydrogenation in liquid phase, in slurry reactor may present important advantages with respect to the gas phase like better temperature control due to the higher heat capacity of the liquids, thus increasing catalyst life, quality and uniformity of the reaction products. Also saving in catalyst wastage and energy, higher rate of reaction for unit weight of catalyst because of its limited use. These characteristics are of great importance for the increasing production of fine chemicals. Moreover, liquid phase processes are found to give a better selectivity for similar conversion than in vapor-phase processes. Industrial experience with the C_3 cut hydrogenation has widely demonstrated that advantages of liquid phase over the vapor phase in saving vaporization and condensation energy at relatively safe low temperatures.

1.7. PHENOL

Phenol is the common name of hydroxybenzene (C_6H_5OH) and belongs to the class of compounds, commonly referred to as Phenols, containing one or more hydroxyl groups attached to an aromatic ring. The history of phenol goes back to 1834 when it was first isolated from coal tar and named carbolic acid. Now more than 99% of phenol produced worldwide is from synthetic processes.

1.7.1. Physical Properties of the Phenol

At room temperature phenol is a white, crystalline mass. Phenol gradually turns pink if it contains impurities or is exposed to heat or light. It has a distinctive sweet, tarry odor, and burning taste. Phenol has limited solubility in water between 0 and 65^0C. Above 65.3^oC phenol and water are miscible in all proportions. It is very soluble in alcohol, benzene, chloroform, ether, and partially dissociated organics.

Table .1 Physical Properties of Phenol

Property	Value
Molecular weight g/mole	94.11
Boiling point at 101.3 kPa	181.75
Freezing point °C	40.91
Vapor pressure at 25 °C, Mpa	46.84
Flash point (closed cup) °C	79
Density at 20 °C (solid), g/cm^3	1.0722
Critical temperature, °C	421.1
Critical pressure, mPa	6.13
Specific heat at 14-25 °C, J/g.K	2.35
Heat of fusion, J/g	121.54
Heat of vaporization, at bp, J/g	528.7
Heat of combustion, kJ/g	-32.468
Viscosity, mPa.s(=cP)at 50, 70, 90 °C respectively	3.49, 2.03, 1.26
Specific heat (solid) at 4.0, and 227 °C respectively	1.24, 1.41
Specific heat (liquid) at 70-74 °C	2.22

1.7.2. Chemical Properties

Phenol's chemical properties are characterized by the influence of the hydroxyl group and the aromatic ring upon each other. Besides being acidic, a significant industrial chemical property of phenol is the extremely high reactivity of its ring toward electrophilic substitution. If steric conditions permit, the substitution leads to the formation of the 2- or 4- mono derivative, then to the 2, 4- or 2 ,6-di derivative, and finally to the 2, 4, 6-triderivative. The halogenation of phenol produces mono-, di- and tri-halophenols.

1.7.3. Manufacture

The cumene oxidation route is the leading commercial process of synthetic phenol production, accounting more than 95% of the phenol produced in the world .The remainder of synthetic phenol is produced by the toluene oxidation route via benzoic acid. Two major producers of phenol in India are Herdillia Chemical, Bombay, and Hindustan Organic Chemicals, Kerala with capacities of 21000 and 40000 tones per year respectively.

1.8. CYCLOHEXANONE

Cyclohexanone is a colorless, mobile liquid with an odor suggestive of peppermint and acetone. Cyclohexanone is chiefly a chemical intermediate and as a solvent fro resins, dyes and insecticides. Cyclohexanone was first prepared by the distillation of calcium pimelatean $OOC(CH_2)_5COOCa^{2+}$, later by the catalytic hydrogenation of cyclohexanol.

1.8.1. Physical Properties

Cyclohexanone is miscible with methanol, ethanol, acetone, benzene, n-hexane, nitrobenzene, diethyl ether, naphtha, and most organic solvents. This ketone dissolves cellulose nitrate, acetate, and ethers, vinyl resins, raw rubber, waxes, fats, oils and many of the organic compounds.

Table 2. Physical properties of the Cyclohexanone

Property	Value
Boiling point	156°C
Melting point	-32.1°C
Relative density (water = 1)	0.95
Solubility in water, g/100 ml at 20°C	8.7
Vapour pressure, Pa at 20°C	500
Relative vapour density (air = 1)	3.4
Relative density of the vapour/air-mixture at 20°C (air = 1)	1.01
Flash point	44°C c.c.
Auto-ignition temperature	420°C
Explosive limits, vol% in air: 1.1 (at 100°C)	-9.4
Octanol/water partition coefficient as log Pow	0.81

1.8.2. Chemical Properties

Cyclohexanone shows most of the typical of aliphatic ketone. Reduction converts cyclohexanone to cyclohexanol or cyclohexane, and oxidation with nitric acid converts cyclohexanone almost quantitatively to adipic acid. Cyclohexanone is used a building block in the synthesis of many organic compounds, such as pharmaceuticals, insecticides, and herbicides and is also used in the manufacture of magnetic tapes.

1.8.3. Manufacture

This ketone is produced commercially by the catalytic hydrogenation of phenol or by the catalytic air oxidation of cyclohexane, and may be prepared by either the catalytic dehydrogenation or oxidative dehydration of cyclohexanol. The hydrogenation of phenol is the most efficient route.

1.9. CYCLOHEXANOL

Cyclohexanol is a colorless, viscous liquid with a camphoraceous odor. It is used chiefly as a chemical intermediate, a stabilizer, and a homogenizer for various soap detergent emulsions. Cyclohexanol was first prepared by the treatment of 4-iodocyclohexanol with zinc dust in glacial acetic acid, and later by the catalytic hydrogenation of phenol at elevated temperatures and pressures.

1.9.1 Physical Properties

Cyclohexanol is miscible in all proportions with most organic solvents. It dissolves many oils, waxes, gums, and resins.

Table 3. Physical properties of the Cyclohexanol

Property	Value
Boiling point	161°C
Melting point	23°C
Relative density (water = 1)	0.96
Solubility in water, g/100 ml at 20°C	4
Vapour pressure, kPa at 20°C	0.13
Relative vapour density (air = 1)	3.5
Relative density of the vapour/air-mixture at 20°C (air = 1)	1.00
Flash point	68°C c.c.
Auto-ignition temperature	300°C
Explosive limits, vol% in air	2.4-12
Octanol/water partition coefficient as log Pow	1.2

1.9.2. Chemical Properties

Cyclohexanol shows most of the typical reactions of secondary alcohols. It reacts with organic acids to form esters, and with acids to form the corresponding halides. Strong oxidizing agents such as nitric acid or alkaline potassium permanganate convert cyclohexanol to adipic acid $HOOC(CH_2)_4COOH$. Oxidation of cyclohexanol to adipic acid is the most important use in the manufacture of nylon 6, 6 polymers of adipic acid and Hexamethylene diamine. Adipic acid may also be used to produce the hexamethylene diamine. The next important usage of cyclohexanol, admixed with cyclohexanone as KA-oil, is in the production of Caprolactam, which is used in the manufacture of nylon-6 polymer.

1.9.3 Manufacture

This alcohol is produced commercially by the catalytic air oxidation of cyclohexane or the catalytic hydrogenation of phenol. The oxidation of cyclohexane to a mixture o cyclohexanol and cyclohexanone, known as KA-oil (ketone-alcohol, cyclohexane-cyclohexanol crude mixture) is used most productions. The hydrogenation of phenol to a mixture of cyclohexanol and cyclohexanone is usually carried out at elevated temperatures and pressures in either the vapor phase catalyzed by nickel or in the liquid phase.

1.10. KA-OIL

The mixture of Cyclohexanone and Cyclohexanol known as KA-oil can be separated by distillation or converted to cyclohexanone by dehydrogenation over either zinc oxide or nickel or magnesium oxide. Mild oxidation of cyclohexanol to cyclohexane can be carried out with or without catalyst.

1.11. SAFETY FACTORS

Handling of chemicals requires adequate care, as some of the chemicals are hazardous to the health . Given below are the chemicals handled in the experiments, and their hazardous levels, and handling.

1.11.1. Phenol

Phenol is toxic if absorbed through the skin and may result in death, even if the exposed area is as small as that of hand or forearm. Contact with skin also cause dangerous and painful burn. Phenol fumes are irritating to the eyes and nose.

Phenol is a local anesthetic; therefore there is no initial pain upon contact and by the time burning is sensed, it has penetrated the skin. Loss in pain does not indicate the removal of phenol from the body. Immediate washing of skin with Ethyl alcohol solution or warm water usually removes the phenol with serious consequences. Eyes should also wash with warm water.

1.11.2. Cyclohexanol and Cyclohexanone

Both Cyclohexanol and Cyclohexanone are slightly toxic by the oral route of exposure and slightly irritating to the skin. They can cause severe eye irritation and transient corneal injury. Precaution that should be observed as a matter of course in using Cyclohexanol and Cyclohexanone include adequate and proper ventilation, avoidance of prolonged breathing of vapors or contact of liquid with the skin, avoidance of internal consumption and protection of eyes against splashing liquid.

1.12. REACTION POSSIBILITIES OF PHENOL HYDROGENAITON

Hydrogenation of phenol is one of the complex reactions with chances formation of many by products. Fig.2.2 shows different reaction possibilities and their standard free energies changes (ΔG) (velu, et al.,) .

The free energies of reaction are negative for each of the hydrogenolysis/ hydrogenation steps except that of the partial hydrogenation of benzene to cyclohexene, for which the ΔG is positive. The complete hydrogenation of phenol to cyclohexane is a highly facile reaction.

Partial hydrogenation of phenol may give cyclohexanone while complete hydrogenation gives cyclohexanol. Cyclohexane can be formed by the Hydrodeoxygenation of cyclohexanone (reaction 3), by hydrogenolysis of cyclohexanol (reaction 4) or via cyclohexene (reaction 5 and 6)

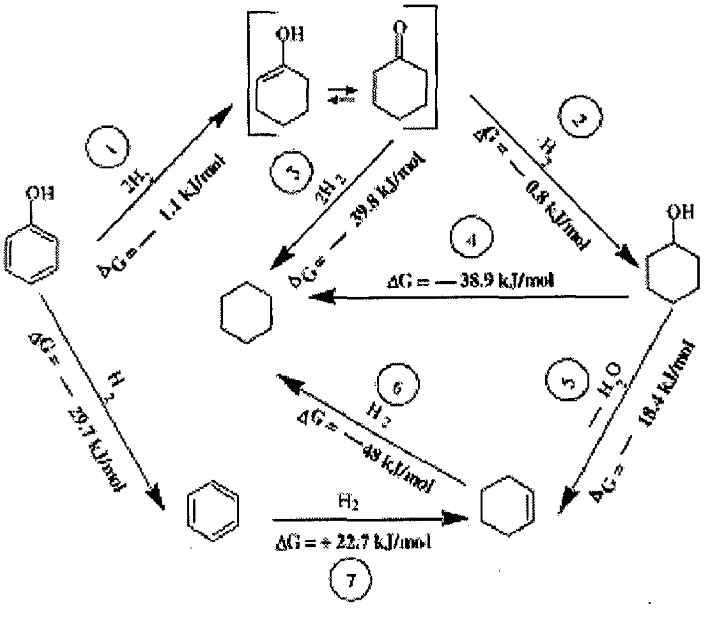

Fig.1.2. Reaction possibilities of phenol hydrogenation

1.7. AIM AND OBJECTIVES

Objective of this work is to hydrogenate phenol completely to cyclohexanone. The aim of this work is to find, how Palladium supported on carbon catalyst affects the liquid phase hydrogenation of phenol. This can be achieved by experimentally finding how palladium catalyst affects conversion and selectivity of the phenol, at different conditions.

CHAPTER 2

THEORY OF THREE PHASE REACTIONS

2.1. GENERAL THEORY

One of the main examples of three phase reactions is heterogeneous catalytic reaction of a liquid and gas reactants. In this type of reactions reactants were catalyzed by a supported metal catalysts.. The general theory of a simple reaction of gas reactant A reacting with liquid phase reactant B catalyzed with a supported catalyst, is discussed below.

Three-phase reaction system can be represented by the reaction scheme

$$A+\nu B \xrightarrow{catalyst} \nu_E E \qquad \ldots\ldots\qquad (2.1)$$

The species A the reactant presents in the gas phase and B is a nonvolatile reactant present in the liquid phase, with the reaction occurring at the surface of a solid catalyst.

A number of steps have to occur before species A can be converted to products on the active sites of the catalyst as given below.

1. Transport of A bulk gas phase to the gas-liquid interface.
2. Transport of A from gas-liquid interface to the bulk liquid.
3. Transport of A and B from bulk liquid to the catalyst surface.
4. Intraparticle diffusion of the reactants in the pores of the catalyst.
5. Adsorption of the reactants on the active sites of the catalyst.
6. Surface reaction of A and B to yield products.

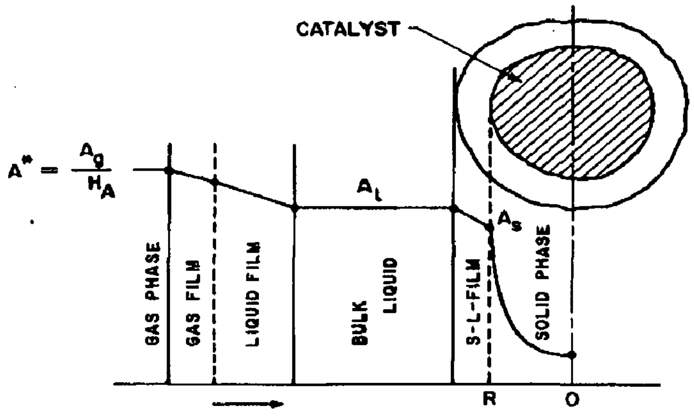

Fig. 2.1 Concentration of gas phase spices A in a three-phase catalytic system.

The concentration profile of species A as it diffuses from the bulk gas to the interior of the catalyst is shown in **Fig.2.1.** Reactor performance analysis can be done first for a differential reactor, in which concentrations of A and B can be assumed to be more or less constant throughout the reactor.

For the case of the liquid phase reactant concentration of B is far in excess of that of the dissolved gas A .The species A now becomes the limiting reactant, for this case rate of reaction based on power law model is now given by

$$\Omega_A = k_m A^m \qquad \ldots\ldots\ldots \qquad (2.2)$$

where k_m is the pseudo m-th order rate constant, $cm^3/g(cm^3/mole)^{m-1}s^{-1}$,and is defined as m.

$$k_m = k_{mn} B_l^n \qquad \ldots\ldots\ldots \qquad (2.3)$$

where B_l is the concentration of B in the bulk liquid,mole/cm^3. Eqn. (2.2) is valid provided B_l is very much greater than the saturation solubility of A in the liquid, that is the equilibrium value corresponding to the gas-phase concentration prevailing in the reactor. Isothermal conditions are assumed for this analysis. Assuming that the catalyst particles are completely wetted and the pores filled with liquid.

The number of steps necessary for the reaction to occur can be divided grossly into two categories:

A) Overall mass transfer from fluid phase to the catalyst surface.

B) Intraparticle diffusion with surface reaction

2.1.1. Overall Rate of Mass Transfer

The rate of mass transfer of species A from gas phase to the surface of the catalyst can be derived from the following relevant equations.

The rate of gas-to-liquid mass transfer in a differential reactor is given as

$$R_A = K_L a_B (A^* - A_l) \qquad \ldots\ldots \quad (2.4)$$

where, R_A is the rate of mass transfer per unit volume of the reactor, mole/cm^3/s;

A^* is the saturation solubility, mole/cm^3;

A_l is the concentration of species A in the bulk liquid,mole/cm^3

$K_L a_B$ is the overall gas-liquid mass transfer coefficient and can be related to the individual gas-side and liquid-side mass transfer coefficients as

$$\frac{1}{K_L a_B} = \frac{1}{H_A k_g a_B} + \frac{1}{k_L a_B} \qquad \ldots\ldots \quad (2.5)$$

where

$H_A$is the Henry's law constant defined as A_g / A^*,

units of H_A are (mole/cm^{3}of gas)/(mole/cm^{3}of liquid)

A_g is the concentration of A in the bulk gas, mole/cm^3

$k_g a_B$ is the gas-side mass transfer coefficient, s^{-1}

$k_L a_B$ is the liquid-side mass transfer coefficient, s^{-1}

a_B is the gas-liquid interfacial area, cm^2/cm^3.

For sparingly soluble gases, such as hydrogen, and for pure gas feeds, the term $K_L a_B$ can be approximated to $k_L a_B$.

The rate of mass transfer from the bulk liquid to the surface of the solid catalyst can be expressed as

$$R_A = k_s a_p \left(A_l - A_s\right) \qquad \ldots\ldots\ (2.6)$$

where

k_s is the liquid-to-particle mass transfer coefficient ,cm/s

a_p is the external surface area of catalyst particles per unit volume of the reactor, cm^2/cm^3

A_s is the concentration of A at the catalyst surface, $mole/cm^3$

The term a_p for spherical particles is given as

$$a_p = \frac{6w}{\rho_p d_p} \qquad \ldots\ldots\ (2.7)$$

where, w is the amount of catalyst per unit volume of the reactor, g/cm^3

ρ_p is the particle density, gm/cm^3.

d_p is the average particle diameter, cm.

Combining Eons (2.4) and (2.6), the overall rate of mass transfer of A from the gas to the external surface of the catalyst can be expressed as

$$R_A = M_A \left(A^* - A_s\right) \qquad \ldots\ldots\ (2.8)$$

where

$$M_A = \left(\frac{1}{K_L a_B} + \frac{1}{k_s a_p}\right)^{-1} \qquad \ldots\ldots\ (2.9)$$

The above equation is valid irrespective of the type of kinetic model.

2.1.2. Rate of Chemical Reaction

In three phase catalytic reactions extrinsic reaction rate depends on many factors. For this kind of reactions reaction kinetics are expressed by either power law or Langmuir-hinshelwood-type kinetics

2.1.2.1. Power law model

For the case of where the Intraparticle diffusional resistance is negligible, and the concentration of A is uniform throughout the catalyst particle, which is equal to A_s. Then the rate of reaction per unit volume is given by

$$R = wk_m A_s^m \qquad \ldots\ldots\ldots \qquad (2.10)$$

The unknown concentration A_s in the above equation can be eliminated using Eqn. (2.8), and the equations for the overall rate in terms of the known parameters can be obtained.

For m-th-order reactions, A_s is obtained from Eqn. (2.10) as

$$A_s = \left(\frac{R_A}{wk_m} \right)^{1/m} \qquad \ldots\ldots\ldots \qquad (2.11)$$

Substituting above in Eqn (2.8) we obtain an implicit equation for R_A as

$$R_A = M_A \left[A^* - \left(\frac{R_A}{wk_m} \right)^{1/m} \right] \qquad \ldots\ldots\ldots \qquad (2.12)$$

the above equation can be solved by a trail and error procedure to predict R_A.

where η_c is catalytic effectiveness factor which defined as

$$\eta_c = \frac{r_A}{r_{\max}} \qquad \ldots\ldots\ldots \qquad (2.17)$$

where r_A is the rate of the reaction and $r_{\max}$ is the maximum rate of reaction in the catalyst particle based on A_S.

η_c for the general case of nonlinear kinetics is given by

$$\eta_c = \frac{1}{\phi}\left(\coth 3\phi - \frac{1}{3\phi}\right) \qquad \ldots\ldots\ldots \qquad (2.18)$$

where ϕ is generalized Thiele modulus for non linear and m-th-order reaction is given by

$$\phi = \frac{R}{3}\left[\left(\frac{m+1}{2}\right)\frac{\rho_p k_m A_s^{m-1}}{D_e}\right]^{1/2} \qquad \ldots\ldots\ldots \qquad (2.19)$$

Except for the case of m = 1 Thiele modulus ϕ is a function of the concentration A_s. A trail and error procedure is necessary to calculate R_A from Equations (2.8) and (2.15).

2.1.4. Overall Effectiveness factor

The concept of overall effectiveness factor is useful in simplifying the calculation of the rate of reaction in a three-phase system. An overall effectiveness factor for a three phase reactor can be defined as the actual rate of reaction divided by the rate obtained by neglecting all the transport resistances.

2.1.4.1. Analytical solutions for power law kinetics

Using power law kinetics, overall effectiveness factor is given as

$$\eta = \frac{R_A}{w\Omega_A\left(A^*\right)} \qquad \ldots\ldots\ldots \qquad (2.20)$$

For m-th-order reaction, the above definition of η gives

$$\eta = \frac{R_A}{wk_m\left(A^*\right)^m} \qquad \ldots\ldots\ldots \qquad (2.21)$$

Overall effectiveness factor also represents the efficiency of the reactor .When $\eta \to 1$, the reactor operates at maximum efficiency, while in the presence of transport resistances, η will be less than unity.

In order to obtain an analytical solution for η in terms of known parameters, the unknown surface concentration of A (A_s) has to be eliminated in Equations (2.8)and(2.15), and in the definition of ϕ in Equation (2.18). This can be done by expressing the surface concentration A_S in terms of overall effectiveness factor. From Equation (2.8) and the definition of η given above

$$a_s = 1 - \frac{\eta}{\sigma_A} \qquad \ldots\ldots\ldots \qquad (2.22)$$

where

$$\sigma_A = \frac{M_A A^*}{w\Omega_A\left(A^*\right)} \qquad \ldots\ldots\ldots \qquad (2.23)$$

$$\sigma_A = \frac{M_A}{wk_m\left(A^*\right)^{m-1}} \quad \text{for m-th-order} \qquad \ldots\ldots\ldots \qquad (2.24)$$

and a_s is the dimensionless surface concentration of A, which is equal to A_s/A^*.

σ_A is a dimensionless parameter characterizing the external mass transfer that is from gas to liquid and liquid to solid .This represents the ratio of maximum possible rate of mass transfer to the maximum rate of chemical reaction. Substituting for a_s from Equation (2.22) in (14) and using the definition of η from Equation (2.21) we get

$$\sigma_A\, \eta = \eta_c \left(1 - \frac{\eta}{\sigma_A}\right)^m \qquad \ldots\ldots\ldots \qquad (2.25)$$

Substituting for η_c from Equation (18), we get

$$\eta = \frac{1}{\phi}\left(\coth 3\phi - \frac{1}{3\phi}\right)\left(1 - \frac{\eta}{\sigma_A}\right)^m \qquad \ldots\ldots\ldots \qquad (2.26)$$

The generalized Thiele modulus ϕ can also be expressed in terms of overall effectiveness factor η, using Equation (2.21) in Equation (2.18). Thus

$$\phi = \frac{R}{3}\left[\left(\frac{m+1}{2}\right)\frac{\rho_p k_m \left(A^{*}\right)^{m-1}}{D_e}\left(1-\frac{\eta}{\sigma_A}\right)^{m-1}\right]^{1/2} \qquad \cdots\cdots \qquad (2.27)$$

That is

$$\phi = \phi_o\left(1-\frac{\eta}{\sigma_A}\right)^{(m-1)/2} \qquad (2.28)$$

The parameters ϕ_o is a Thiele modulus based on equilibrium solubility A^{*}, which is known quantity and is by

$$\phi_o = \frac{R}{3}\left[\left(\frac{m+1}{2}\right)\frac{\rho_p k_m \left(A^{*}\right)^{m-1}}{D_e}\right]^{1/2} \qquad \cdots\cdots \qquad (2.29)$$

Substituting for ϕ in Equation (24), we obtain a nonlinear algebraic equation for the overall effectiveness factor of a three phase reactor for power-law kinetics.

$$\eta = \frac{\left(-\frac{\eta}{\sigma_A}\right)^{(m+1)/2}}{\phi_o}\left\{\coth\left[3\phi_o\left(1-\eta/\sigma_A\right)^{(m-1)/2}\right]-\frac{1}{3\phi_o\left(1-\frac{\eta}{\sigma_A}\right)^{(m-1)/2}}\right\} \qquad \cdots\cdots \qquad (2.30)$$

The above Equation is implicit in η and has to be solved by a trail and error method. Standard methods for the solution of nonlinear equations, such as the Newton-Raphson iteration, can be used.

The general accepted theory of hydrogenation is that all reactants are adsorbed at active sites on the surface of the catalyst and that reaction is between adsorbed molecules.

One of the most important conditions for successful hydrogenation is good contact between that portion of the molecule to be reduced and the surface of the catalyst.

2.2. FACTORS EFFECTING THREE PHASE REACTIONS

Factors effecting the hydrogenation reactions are temperature, pressure, concentration of reactants and catalyst and characteristics of the catalyst.

2.2.1. TEMPERATURE

Reaction temperature will affect the rate and extent of hydrogenation as it does any chemical reaction. At times an increase in temperature can be detrimental to a reduction process (because it may lead to loss of selectivity if a second functional group is present.)

2.2.2. PRESSURE

Hydrogen pressure another form of energy, can be beneficial as well as detrimental. An increase in pressure from several atmospheres to higher pressure will decrease reaction time considerably

2.2.3. SOLVENT

Reductions can be done carried out in the absence of solvent when the material to be reduced is a liquid or a low melting solid. However, reaction generally proceeds more rapidly in most solvents. Their presence helps to modify and allows better control of exothermic reactions. They are usually chosen for the ability to dissolve the compound to be reduced.

2.2.4. AGITATION

Some form of movement of the catalyst in the reaction medium is necessary in order for reduction to take place. It was found that in all reductions, hydrogen adsorption comes to a halt when agitation by any means is stopped. Cessation of mixing will keep an exothermic reaction under control.

2.2.5. CATALYST SUPPORT

A support results in more catalytic surface area and allows more economical use of the metal. On commercial scale mechanical loss of metal can be minimized when supported catalysts are employed. The financial savings are substantial when noble metals are used, since the recovered catalysts are returned to the manufacturer for credit. There were reports which show, on an equal weight of metal basis, that reduction proceeds more rapidly with Supported Catalyst than with the metal itself.

2.3.THREE PHASE REACTORS

Liquid phase hydrogenation process involves three phases, hydrogen in gas phase, component to be hydrogenated in liquid phase and catalyst in solid phase. In most applications, the reaction occurs between a dissolved gas and a liquid-phase reactant in presence of the solid catalyst. Basically there are two types of three phase catalytic reactors

Types of three phase reactors

A) Fixed-Bed Reactors

B) Slurry Reactors

2.3.1. Fixed-Bed Reactors

In this type of reactor, the two fluid phases move over a stationary bed of catalyst particles. This can be operated as

1. Co current down flow of both gas and liquid (trickle-bed reactor)

2. Down flow of liquid and countercurrent up flow of gas
3. Co current up flow of both gas and liquid.

2.3.2. Slurry Reactors

In this type particles are in a suspended state. Depending on the mode by which the catalyst particles are suspended, it is possible to classify these reactors into three categories.

1. Mechanically agitated slurry reactors
2. Bubble column slurry reactors
3. Three-phase fluidized-bed reactors

2.3.2.1 Mechanically Agitated Slurry Reactors

In this catalyst particles are kept in suspension by means of mechanical agitation

2.3.2.2. Bubble Column Slurry Reactors

In this the particles are suspended by means of gas-induced agitation. Relatively small particles are used in this type of reactor.

2.3.2.3. Three-Phase Fluidized-Bed Reactors

In this the particles are suspended because of the combined action of bubble movement and cocurrent liquid flow.

2.4. SELECTION OF THE REACTOR FOR THE EXPERIMENT

Since heat transfer is more efficient in slurry reactors, the control of temperature is easy in slurry reactors. This leads to uniform temperature at the active sites of the catalyst and avoids formation of hot spots. Large liquid hold ups in slurry reactors also facilitates better temperature control due to the large heat capacity of the liquid phase. Catalyst handling is also easy in slurry reactors.

2.5. EVALUATION OF PARAMETERS FROM THE EXPERIMENTAL DATA FORM THE SLURRY REACTOR

Methods for determining the kinetic parameters of three phase reactions using power law model was given below

2.5.1. Determination of Kinetic Parameters

It is preferable to carry out kinetic studies under conditions such that the mass transfer and other complex effects are absent. Agitated slurry reactor is the most suitable type for studying reaction kinetics. Operating this reactor at sufficiently high agitation speeds can often eliminate the external mass transfer resistance. Similarly, very small catalyst particles can be used in this reactor, thereby minimizing the intraparticle concentration gradients. Also, isothermal conditions can be easily being achieved due to high heat transfer efficiency.

2.5.2. Interpretation of Experimental Rate Data

To evaluate the intrinsic kinetic parameters from the measured rates, it is necessary to know the extent of the contribution of various diffusional resistances. This can be done provided the mass transfer parameters $K_L a_B$, k_s and D_e are obtained by independent experiments for the same system or calculated using suitable correlations. When the observed rate is very much smaller than the maximum rate of gas-liquid mass transfer, it can be assumed that this resistance is negligible. The ratio of these rates is given by $R_A / K_L a_B A^*$. If this quantity is less than 0.1, gas-liquid mass transfer resistance may be assumed to be absent, while close to unity, it represents a case of gas-liquid mass transfer control. In an experimental program using an agitated reactor, it may be possible to eliminate this resistance by in creasing the stirrer speed. On similar grounds, the ratio $R_A / K_s a_p A^*$ determines the contribution of liquid-solid mass transfer. If the ratio is less than 0.1, it can be assumed that the liquid-solid mass transfer resistance is negligible.

The effect of intraparticle diffusion for a m-th-order reaction can be considered negligible provided that the following criterion based on the experimental rate is satisfied.

$$\frac{R}{3}\left(\frac{m+1}{2D_e}\frac{\rho_p R_A}{wA_s}\right)^{1/2} < 0.2 \qquad \ldots\ldots\ (2.31)$$

The surface concentrations A_s and B_s are given as

$$A_s = A^* - \frac{R_A}{M_A} \qquad \ldots\ldots\ (2.32)$$

$$B_s = B_l - \frac{\nu R_A}{k_s a_p} \qquad \ldots\ldots \qquad (2.33)$$

If liquid-solid or intraparticle diffusion resistance is significant, the experiments should be conducted at lower particle size to minimize these resistances.

In order to determine the reaction order with respect to the gaseous component, the experimental rate data must be obtained at different concentrations of A. at constant concentration of B, and other conditions. This can be done by either using an inert diluent or varying the total pressure in the reactor. A plot of $\log R_A$ vs $\log A_S$ will have a slope equal to the value of reaction order m, provided that intraparticle gradients are not significant. If the external mass transfer resistance is negligible, $A_S=A^*$ and, in such cases, $\log R_A$ vs $\log A^*$ can be directly plotted to obtain m. To determine the order with respect to B, experiments at different concentrations of B must be carried out keeping the pressure and the other conditions constant. Then, plot of $\log R_A$ vs $\log B_S$ will have a slope equal to n. Once m and n are known, the reaction rate constant k_{mn} can be calculated using the equation

$$R_A = w k_{mn} A_s^m B_s^n \qquad \ldots\ldots \qquad (2.34)$$

The activation energy E can be obtained from the rate constant values observed at different temperatures. A plot of $\ln k_{mn}$ vs $1/T$ should be a straight line with slope equal to $-E_a/R_g$. As the temperature is increased, the diffusional effects may become important, and the criteria suggested earlier should be checked at each data point to ensure that the process is controlled by chemical reaction at all the temperatures studied.

CHAPTER 3

LITERATURE REVIEW

3.1. LIQUID PHASE

In the recent past only there are two studies reported on the liquid phase hydrogenation of phenol.One is Velasco et *al*, (1995) and another work done by the Miguel at *al*.(1994). The former have studied the preparation and calcination of palladium on alumina catalyst in the hydrogenation of phenol. While later's study is on the preparation of platinum on alumina, catalyst. Aubert, at *al*.(1988) have studied the hydrogenation of substituted benzenes and Hilton A. Smith A.H et *al*., (1961) have studied the hydrogenation of phenol with platinum and rhodium catalysts.

Velasco et *al*. (1995) have studied phenol hydrogenation in liquid phase slurry reactor. Catalysts were prepared by adsorption from an aqueous solution of palladium dichloride in hydrochloric acid on a commercial AL- 3945 support. Some of the precursors prepared were calcined after drying at 773 K for four hours in air referred as calcined catalysts and some just heated at 423 K for one hour in nitrogen referred as noncalcined catalyst.

Characteristics of the prepared catalysts:

Calcined catalysts: size of the particles ranged 0.08-0.40 mm, actual Pd contents 0.19-0.94; dispersion 0.91-1.12;

Non calcined catalysts: size of the particles ranged 0.08-0.16 mm, actual Pd content 0.19-0.94; dispersion 0.72-1.25;

Catalytic activity was determined for the liquid phase hydrogenation of phenol in a cylindrical stirred tank reactor, the reactor was operated in a semi continuous way, bubbling 50 cm^3/min of pure hydrogen in 200 cm^3 of the liquid feed.

The temperature and pressure maintained constant during the each experiment. From the experimental results it has been found that the there is no formation of the cyclohexanol at the beginning of the reaction

Kinetic regime was obtained with the stirring speed 750rpm and a catalyst particle size of 0.08-0.16mm.

Considering chemical reaction controls the rate and hydrogen adsorption occurs dessociativly, activities measured at constant conversion of phenol at very low formations of cyclohexanone and cyclohexanol were given as,

$$TOF_{ph} = K_1 P_{H_2}{}^2 / (K_2 + K_3 P_{H_2}{}^{0.5})^n \qquad (3.1)$$

Where n is the number of active sites involved in the limiting step, and k_1, k_2, and k_3 are constants for the particular conditions. And working under at relatively small hydrogen pressures, above equation is simplified to a equation of second order dependence of activity with the hydrogen partial pressure

$$TOF_{ph} = K_1^1 P_{H_2}{}^2 \qquad (3.2)$$

This shows a second order dependence of activity with hydrogen partial pressure.

Where as among the calcined and non calcined catalysts, calcined catalysts despite their higher metallic dispersion, presented lower activity than their corresponding non calcined catalysts. Among the latter series, catalysts with 0.5% pd presented 4 times the activity expected assuming a linear correlation activity –surface palladium content.

Effect of the temperature was also examined and the activation energy for hydrogenation of phenol to cyclohexanone was given as 56.8 kJ mol^{-1}. Selectivity to cyclohexanone was found to be very high for all experiments, and increased with the temperature. That is the apparent activation energy of the cyclohexanone formation from phenol is higher than apparent activation energy of cyclohexanone hydrogenation to cyclohexanone.

Miguel et *al.* (1994) have studied hydrogenation of phenol in liquid phase has been studied. In their study they have prepared a series of Platinum/ alumina catalysts by means of adsorption and anionic exchange in aqueous solution of hexachloroplatinic acid. A commercial γ- alumina has been used as a catalyst support. The actual platinum content of the prepared catalysts varied from 0.63-0.81wt.% , catalyst particle size range being 30-235 μm and dispersion range is 0.82-1.19.

Kinetic experiments were conducted in a stirred tank reactor. Methylcyclohexane was used as the solvent for the phenol. Hydrogen was continuously bubbled in the reactor. The experiments were run at constant temperature and pressure with different levels of agitation.

In the kinetic regime the products formed are cyclohexanone and cyclohexanol only. It had been found that activity for phenol hydrogenation increases almost linearly as the hydrogen partial pressure increases in their studied range. Selectivity was found to decrease as hydrogen partial pressure was increased thus favoring cyclohexanol formation. The also found that the hydrogen is the first reactant that present mass transfer limitations.

Their study on the influence of temperature on the activity and selectivity showed that selectivity increased as the operating temperature was increased, thus favoring cyclohexanone formation. And the apparent activation energies for phenol consumption, 27.44 kJ mol^{-1}; for cyclohexanone formation 35.55 kJ mol^{-1} and for cyclohexanol formation , 21.93 kJ mol^{-1}.

Aubert et *al.* (1988) have studied the hydrogenation of substituted benzenes (R= Et, Ph, c-C_6H_{11}, $PhCH_2$, c-$C_6H_{11}CH_2$), of *ortho* and *para* – substituted phenols (R=Et, Ph, c-C_6H_{11}, $PhCH_2$) was studied by a batch method at 340°C and 70 bar H_2 over sulfided NiO-MoO_3/γ-Al_2O_3 catalyst.

The hydrogenating activity is closely dependent on the aromaticity of the system to be hydrogenated through the more or less important delocalizatin of π-electrons resulting from the electron donating ability of OH or NH_2 groups by resonance.

The lower reactivity observed for hydrogenation of *ortho-* and *para-* substituted phenols than that of phenol itself would appear to result from electronic effects rather than steric ones. The hydrocraking activity observed during the course of hydroprocessing of phenols is still dependent on the aromatic character of the system and π-electron delocalization.

Smith et *al.* (1961) have studied the catalytic hydrogenation of phenol, catechol, resorcinol, hydroquinone, phloroglucinol and pyrogallol has been studied with platinum and rhodium catalysts.

The rates of hydrogenation at 30° C for the hydroxybenzenes using 5 % rhodium –on-alumina show the same general effect of symmetry as observed for the corresponding compounds with platinum.

Activation energies were calculated from the "least squares" slopes activation energy plots. For each compound the activation energy was greater for hydrogenation with the supported rhodium catalysts than with Adams Platinum. The low rate constants and high activation energies for phloroglucinol may be attributed to resonance stabilization of this compound in the keto form.

The following reaction mechanism is suggested. The hydroxybenezene, phenol for example, is adsorbed on the catalyst surface where hydrogenation takes place to give hydroxycyclohexenes as short-lived intermediates. These short lived intermediates may or may not be desorbed from the catalyst surface, that is the hydroxycyclohexene may react with an additional mole of hydrogen to give a cyclohexanol without desorbing in to the reaction mixture where it would compete with the unreacted phenol for adsorption. The intermediate hydroxycyclohexene may undergo clevage to cyclohexene and water, ring hydrogenation to give cyclohexanol. The reactions probably occur simultaneously until the double –bonded molecules are saturated.

Three hydroxycyclohexene intermediates are possible. The 1-hydroxycyclohexene-1 is the tautomeric form of cyclohexanone. This tautomerization would be expected to take place since the keto form is more stable than the enol form by about 18kcal.mol^{-3} $^{\text{(check)}}$ This could account for the presence of ketones in the reaction mixtures without claiming that cyclohexanone is a reaction intermediate in the usual sense.

3.2. VAPOR PHASE

Sheldon G. Shore et al.,(2004) have studied the catalytic gas phase phenol hydrogenation activities/selectivities associated with Pd/SiO_2 prepared by $Pd(NO_3)_2$ and $Pd(C_2H_3O_2)_2$ impregnation have been compared with those delivered by $Pd–Yb/SiO_2$ prepared from a $\{(DMF)_{10}Yb_2[Pd(CN)_4]_3\}_\infty$ precursor. The Pd metal loading spanned the range 1–10% (w/w) and the reaction was conducted over the temperature interval 398–448 K.

In the hydrogenation of phenol over Pd/SiO_2 and $Pd–Yb/SiO_2$, the presence of Yb has a significant impact on catalytic activity and selectivity. In the case of the supported monometallic Pd, use of palladium acetate or nitrate as the metal precursor has little effect on catalyst performance. The presence of Yb served to enhance phenol conversion, an effect that extends to silica supported Ni. A pseudo-first order kinetic analysis combined with TEM characterization has been used to deliver specific rate constants that were slightly lower for larger metal particles; the average Pd particle sizes spanned the range 2–8 nm for 1% to 10%, w/w Pd. While Yb/SiO_2 did not exhibit any hydrogenation activity the specific rates associated with the Pd–Yb bimetallic systems were appreciably greater than the monometallic Pd/SiO2 at each Pd loading. This Pd–Yb synergistic effect is tentatively attributed to a greater availability of reactive hydrogen from surface Yb hydride species. The Yb component in $Pd–Yb/SiO_2$ is present as a thin coating with no evidence of distinct Yb particle formation or, on the basis of XPS analysis, disruption to the Pd site electron density.

A decrease in the effective contact time lowered fractional conversion (over each catalyst) with a preferential formation of cyclohexanone. Where the contact time was maintained constant, an increase in reaction temperature lowered both conversion and cyclohexanone selectivity.

Unnikrishnan R. Pillai, et *al.*,(2004) The effect of strontium promotion is studied for a series of supported palladium catalysts such as Pd/zeolite-b, Pd/Al_2O_3, Pd/SiO_2, Pd/ hydrotalcite and Pd/MgO. Strontium is found to be an effective promoter for enhancing the metal area, percentage dispersion of the metal and therefore the hydrogenation activity of the different supported palladium catalysts with varying acid/base properties. The effect of addition of Sr and Pd onto the support by simultaneous and sequential impregnation methods is studied besides the effect of Sr/Pd ratio.

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Strontium is found to be an efficient promoter for different supported palladium catalysts. Sequential impregnation of Sr and Pd is found to be more effective for the alumina, silica, magnesia and hydrotalcite supported palladium catalysts, whereas simultaneous impregnation of Sr and Pd is more effective for zeolite-b supported catalyst. This is attributed to the microporous nature of the zeolite support that causes the migration of Sr to its micropores thereby making them partly unavailable for the promotional effect if added first. Addition of Sr improves the available metal area and metal dispersion of palladium resulting in an enhanced catalytic activity. Sr-promotion also enhances the basicity of the catalysts. TPR studies suggest that the presence of Sr could also lead to a change in the net electron density at the metal and this could lead to an enhancement in hydrogen adsorption and hydrogenation activity of the catalysts.

Therefore, a combined effect of electronic and physical changes may be responsible for the promotional effects of Sr on supported palladium catalysts.

Park, C et *al.*,(2003) The catalytic action of 10% w/w Pd supported on two forms of graphitic carbon nanofibers (GCN) has been assessed and compared with the performance of 10% w/w Pd on SiO_2, Ta_2O_5, activated carbon (AC), and graphite. Palladium nitrate was used as metal precursor in each case and the role of the starting metal salt was also considered by examining the action of palladium acetate impregnated SiO_2. The activated catalysts have been characterized by hydrogen chemisorption, high-resolution transmission electron microscopy, and scanning electron microscopy. Phenol hydrogenation was used for testing the catalysts.

Impregnation and activation of (10% w/w) Pd on various oxide and carbon-(including novel GCN) based substrates have led to significant variations in the intrinsic catalytic phenol hydrogenation activity/selectivity. The Pd phase exhibited a morphological diversity where the average Pd particle sizes spanned the range 6–17 nm. A pseudo-first order kinetic analysis has been used to deliver specific rate constants that are indicative of a degree of structure sensitivity in that the intrinsic rate was higher for those systems exhibiting SMSI and increased in the following sequence: Pd/AC ~ Pd/GCN-1 < Pd/GCN-2 < Pd/SiO_2 ~ Pd/graphite < Pd/Ta_2O_5. In the case of Pd/SiO_2, the use of palladium acetate or nitrate as the metal precursor has little effect on catalyst productivity. Variations in selectivity were ascribed to differences in Pd/support interaction(s) that impact on the supported Pd microstructure where, in the case of Pd dispersed on AC and Ta_2O_5, the metal can be considered to adopt a crystallographic orientation that favors partial hydrogenation to cyclohexanone whereas Pd on GCN promotes complete hydrogenation to the alcohol. A decrease in the effective contact time (at constant *T)* lowered fractional conversion with a preferential formation of cyclohexanone. Where the contact time was maintained constant an increase in reaction temperature lowered both conversion and cyclohexanone selectivity (with the exception of Pd/AC and Pd-GCN-1), a result that is ascribed to desorption phenomena.

Velu at *al.*, (2003), Mesoporous CeO_2 and ZrO_2 were synthesized using hexadecyltrimethyl ammonium bromide (C^{16}TMABr) as the template. Their physicochemical properties were investigated using X-ray diffraction (XRD) and N_2 adsorption–desorption methods. Palladium (Pd) 1–10 wt.% was loaded on the mesoporous CeO_2 and ZrO_2 by deposition precipitation method. The Pd metal surface area, dispersion and crystallite sizes were determined by room temperature H_2 chemisorption on reduced samples. The catalytic activity of Pd supported mesoporous CeO_2 (Pd/CeO_2-MS) and ZrO_2 (Pd/ZrO_2-MS) were evaluated for the first time in the vapor phase hydrogenation of phenol in the temperature range between 160 and 230 °C at atmospheric pressure. Vapor phase hydrogenation of phenol over Pd supported on mesoporous CeO_2 and ZrO_2 lead to the following conclusions:

(1) An appreciable catalytic performance in terms of phenol conversion and cyclohexanone selectivity can be obtained over catalysts with 1–3 wt.% Pd loading.

(2) Under identical experimental conditions, the catalytic activity over mesoporous CeO_2 and ZrO_2 supports is better than that obtained over MgO, Al_2O_3 or MgO-Al_2O_3 mixed oxide derived from hydrotalcite as supports.

(3) The Pd/CeO_2-MS exhibits a stable activity during on-stream operation, but produces a mixture of cyclohexanone (about 50%), cyclohexanol (about 35%) and cyclohexane (about 15%) with a phenol conversion of about 80% at 180 °C. On the other hand, Pd/ZrO_2-MS produces exclusively cyclohexanone (above 90%), but undergoes deactivation.

(4) The observed selectivity difference has been attributed to the difference in the mode of phenol adsorption. In Pd/CeO_2-MS, coordinatively unsaturated Ce4+ ions formed as a result of partial surface reduction of CeO_2 to CeO_{2-x} or Ce_2O_3-like non-stoichiometric oxide, which acts as Lewis acidic sites. Phenol adsorbed on these Lewis acidic sites leads to the formation of cyclohexanol. On the other hand, in Pd/ZrO_2-MS, the basicity is predominant over acidity, and the phenol adsorbed on basic sites produces cyclohexanone.The surface OH groups formed as a result of the adsorption of H_2 introduce Brönsted sites and carbon deposition on these sites leads to the activity decay. Possible mechanisms for the formation of cyclohexanone and cyclohexanol were given. cyclohexanone can be formed if phenol is adsorbed non-planar to the surface and cyclohexanol can be obtained if it is adsorbed co-planar to the surface.

Scirè, S et *al.*,(2002) The gas-phase selective hydrogenation of phenol to cyclohexanone has been investigated over supported Pd catalysts in order to clarify the role of the support, the Pd precursor and the addition of Ca in controlling activity, selectivity and stability of the catalytic system.

On the basis of the results reported in this paper, it can be concluded that the catalytic behavior of supported Pd catalysts towards the selective hydrogenation of phenol to cyclohexanone is strongly affected both by the acidity of samples and by the electron surroundings of metal active sites (Pd). In particular it can be reasonably suggested that the acid–base properties of the catalysts have a strong influence on the adsorption–desorption equilibrium of reactants and products, being responsible to direct the selectivity towards the reaction products. The catalytic activity of the system appears to be, instead, controlled mainly by the state of the palladium sites on which H_2 is activated. Finally the deactivation rate of the catalyst is strongly dependent on the presence of strong acid sites.

Mark A. K., et. *al.*(2002),the catalytic activity/selectivity of a 5% w/w Pd/SiO_2 catalyst prepared by $Pd(NO3)_2$ impregnation has been compared with that delivered by 5% w/w Pd/SiO_2 and Pd-Yb/SiO2 prepared from $Pd(C_2H_3O_2)_2$ and $\{(DMF)_{10}Yb_2[Pd(CN)_4]_3\}_\infty$ precursors, respectively; phenol hydrogenation (T = 423 K) was used as a test reaction. The activated catalysts have been characterized by HRTEM/EDX; differences in activity are related to the TEM derived Pd particle size distribution.

A pseudo-first-order kinetic analysis supports the following order of increasing phenol hydrogenation activity: Pd/SiO_2-II < Pd/SiO_2-I << Pd-Yb/SiO_2. Taking the monometallic catalysts, the lower phenol conversions delivered by Pd/SiO_2-II can be attributed to the greater presence of electron deficient Pd particles (<2 nm) that are known to exhibit lower inherent hydrogenation activities. The Yb component in Pd-Yb/SiO_2 is present as a thin coating with no evidence of distinct Yb particle formation although there appears to be some intimate contact with the Pd phase. The bimetallic Pd-Yb system delivered appreciably higher phenol conversions, an effect that can again be linked to the d-character of the Pd sites where electron donation from Yb translates into a more effective surface activation of the reactants. Higher phenol conversions invariably lead to a greater selectivity in terms of complete hydrogenation to cyclohexanol. While the presence of Yb elevated conversion, selectivity in terms of the partially hydrogenated cyclohexanone was such that the overall yield of cyclohexanone was significantly enhanced. Addition of a lanthanide shows promise as a means of promoting the production of the high value ''target'' cyclohexanone from supported Pd.

Vishwanathan et *al.*,(2001) have studied gas phase hydrogenation of phenol in the range 523-573 ° K using 1 wt.%Pd/Al_2O_3 and 1 wt.%Ni/SiO_2 catalysts doped with Group I and II promoter oxides. Its found that the charge transfer capacity (CTC) of the promoter oxides on phenol hydrogenation In both Pd – and Ni – based catalysts there is a clear dependence of activity on CTC where phenol hydrogenation rate was elevated with increasing CTC of alkali and alkaline earth metal dopants. Selectivity over Pd/ Al_2O_3 is largely insensitive to the presence of these promoters and the selective hydrogenation to cyclohexanone predominates. In the case of Ni/SiO_2, electron transfer from the promoter, in raising the overall hydrogenation rate favors complete hydrogenation to cyclohexanol but as a significant limiting effect on the degree of hydrogenolysis to benzene.

Mahata and **Vishwanathan** (2000) $Pd(OOCCH_3)_2$, $PdCl_2$, and $Pd(NH_3)_4Cl_2$ precursors were used to study the influence of palladium precursors on structural properties and phenol hydrogenation characteristics of Al_2O_3- and MgO-supported palladium catalysts.

Palladium dispersion in a supported catalyst depends considerably on the precursor as well as on characteristics of the support. $Pd(OOCCH_3)_2$ offers better dispersion of Pd than $PdCl_2$ or $Pd(NH_3)_4Cl_2$ over Al_2O_3 and MgO. Palladium dispersion is higher over MgO-based catalysts compared to Al_2O_3-based catalysts with their respective precursors, which can be attributed to the stronger interaction of Pd with MgO. $Pd(NH_3)_4Cl_2$ leads to lower dispersion of Pd, probably due to the presence of inherent NH_3 (a reducing agent) and facile surface mobility of the precursor. All of the catalysts originating from chlorinated precursors (either $PdCl_2$ or $Pd(NH_3)_4Cl_2$) retain a considerable amount of chlorine on the support even after calcination/ reduction. In addition, Pd particles in Pd/Al_2O_3, originating from $PdCl_2$, also retain some chlorine after the same pretreatment. The absence of residual chlorine in the Pd particles in the other catalysts originating from chlorinated precursors was discussed. Phenol hydrogenation activity over the catalysts is a direct function of the available palladium area. However, residual chlorine in the metal particles or at the metal– support interface reduces activity.

Pd precursors do not have a significant influence on the product distribution of phenol hydrogenation. Al_2O_3- based catalysts are totally selective for cyclohexanone production. MgO-based catalysts produce cyclohexanone, the main product, as well as cyclohexanol, a minor product. Correlations between phenol conversion and product selectivity/ yield revealed that the changes in product selectivity may not be merely due to a change in the overall conversion, and one product does not form at the expense of another. Formation of cyclohexanol along with the main product cyclohexanone is attributed to the strong basicity of MgO. A fraction of the strongly bound phenol, in the form of phenolate, undergoes complete hydrogenation to cyclohexanol before desorption. Acidic sites present over Al_2O_3 causes severe deactivation of the Pd/Al_2O_3 catalysts, while MgO-based catalysts show strong resistance to deactivation.

Shin E.J., et *al.*,(2000) The gas phase hydrogenation/ hydrogenolysis of alcoholic solutions of phenol between 423 and 573° K had been studied using a zeolite- supported catalyst (2.2% w/w Ni). This is a viable means of treating concentrated phenol streams to generate recyclable raw material.

It was concluded that at steady state conversion of phenol, cyclohexanone and cyclohexanol is readily achieved with no appreciable deactivation over Ni/SiO_2 and the product yield is essentially time-invariant. Phenol conversion as a function of molar feed rate can be adequately represented by pseudo-first– order kinetics where the specific rate constant increased with increasing nickel particle size, diagnostic of a structure sensitive reaction.

An increase in nickel loading in the case of Ni/SiO_2 was accompanied by an increasing hydrogenolytic character which can be linked to difference in H_2-TPD (Temperature programmed desorption) and suggestive of a contribution of spillover hydrogen to hydroxygenation. The selectivity trends in terms of hydrogen cleavage versus hydrogen addition extend to the conversion of cyclohexanone and cyclohexanol. Ni/ Na-Y only promote the acid-catalyzed conversion and exhibit an inherent hydrogenolytic character to generate benzene, cyclohexene, and cyclohexane from a hexanolic feed. Conversion of phenol is accompanied by a short-term loss of activity that can be attributed to a pore-blocking effect. Ni/SiO_2 can be effectively used to promote the gas phase treatment of mixed aqueous/methanolic phenol solutions where process selectivity is strongly dependent on water content.

Narayanan, et *al.*, (2000) Hydrotalcites and hydrotalcite-like compounds, having Zn^{2+} and Li^+ as brucite layer cations are prepared. They are tested as supports to disperse palladium and for selective hydrogenation of phenol to cyclohexanone. Effect of the temperature of calcinations was also studied. The hydrotalcite materials and palladium catalysts are characterized by XRD, IR, DTA, BET surface area and CO uptake measurements.

Hydrotalcites were prepared with different Al(III)/Al(III)+Mg(II) ratios at high pH conditions. Palladium is well dispersed in the catalysts prepared by both impregnation and ion-exchange methods over uncalcined hydrotalcite supports. The surface area increases with Al(III)/Al(III)+Mg(II) in calcined hydrotalcites. On calcination of hydrotalcites surface area increases up to the calcination of 723 K, beyond which it decreases. CO adsorption gives a measure of Pd dispersion, which can be directly correlated with phenol hydrogenation. The uncalcined hydrotalcites and the hydrotalcites calcined at 1173K showed good Pd dispersion and phenol hydrogenation activity. The selectivity values over Pd/HT and Pd/CHT catalysts were found to be >95%. It is found that the presence of alumina phase increases the Pd dispersion. The Pd/hydrotalcite catalysts having alumina phase and high alumina content showed deactivation with time for phenol hydrogenation. The 1 wt.% Pd/LiAlHT showed similar Pd dispersions, and hydrogenation activities as that of 1 wt.% Pd/HT. ZnHT was found to be not a suitable support for loading Pd.

Narayanan, S., et al., (1999) Hydrotalcites (HTs) are prepared by low supersaturation and high supersaturation methods containing Mg^{2+}. and Al^{3+}. cations in the brucite-like sheets and having interlayer $CO^{2-}{}_3$ anions. Pd/HT with Pd^{2+}. in the brucite layer was also prepared for comparison. Catalysts containing 1 wt% of Pd are prepared by impregnation method using different Pd precursors. HT and Pd on HT samples are well characterised by XRD and surface area analysis. CO chemisorption is used to estimate the dispersion and metal area of Pd. The supported metal catalysts are evaluated for phenol hydrogenation

Palladium hydrotalcite prepared at high supersaturation with Al content of 0.33 (x~0.33) can be used as a good support in uncalcined form for palladium dispersion and the supported palladium catalyst shows good phenol hydrogenation with >90% conversion and selectivity for cyclohexanone. More than the surface area, the brucite structure and the carbonate anions are responsible for the palladium dispersion. Though palladium on crystalline MgO and $MgAl_2O_4$ spinel are also equally active for CO chemisorption and phenol hydrogenation, there is a faster catalytic deactivation with time compared to 1 wt% Pd on uncalcined hydrotalcite. 1 wt% Pd hydrotalcite catalyst with palladium incorporated in the brucite structure during precipitation shows stable dispersion even after high temperature (673-873 K) calcination treatments.

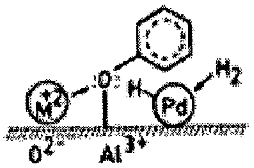
Chen, Y.Z at *al.*,(1999) Calcined Mg/Al hydrotalcites (CHTs) with various atomic ratios of Mg/Al were prepared and used as supports for palladium catalysts.

The result of this study indicated that the Pd/CHT catalysts were effective for selective hydrogenation of phenol to cyclohexanone. The calcined hydrotalcites with the ratio of Mg/Al less than 4 exhibited a large surface area in the range 200-250 m^2/g and were suitable as supports. The base sites of the calcined hydrotalcite were more effective than the acid sites to affect the adsorption form of phenol that was preferentially hydrogenated to cyclohexanone. With a 0.3%Pd/CHT(2) catalyst, a high cyclohexanone selectivity (>95%) with a conversion of 40% was reached. The optimum reaction temperature for cyclohexanone formation was between 160°C and 180°C. The rate of cyclohexanone formation increased with the partial pressure of hydrogen to the order of +2, and decreased with the partial pressure of phenol to the order of -1.

Vishwanathan,V., at al.,(1999) A series of palladium supported on alumina, with Pd variation from 0.5 to 7.0 wt%, was prepared by wet impregnation method and characterized by XRD and CO chemisorption measurements. The catalysts were evaluated for a gas phase hydrogenation of phenol in a fixed-bed reactor at 503 K under normal atmospheric pressure.

From the adsorption measurements, one could infer that phenol hydrogenation depends on the metal dispersion and metal area. Palladium content beyond 3 wt% has no significant effect on the turnover number of phenol hydrogenation. Addition of calcium modifier at a lower concentration, enhances the selectivity for cyclohexanone. Increase in phenol activity of calcium-modified catalyst may result due to the strong interaction between the promoter ion and the adsorbed phenol on the support surface.

A reaction mechanism is proposed wherein the positively charged promoting ion interacts with the oxygen atom of the phenolate to weaken the bond strength between the adsorbed phenol and the support surface, thereby enhancing the rate of desorption of the product



Scheme 1.

Vishwanathan et al., (1998) have synthesized a series of alkali and alkaline earth promoted Pd/Al_2O_3 catalysts by impregnation method, characterised by XRD and CO chemisorption techniques and studied for the vapor phase hydrogenation of cyclohexanone. Its found in their study that the promoted catalysts show higher phenol hydrogenation activity as compared to the unpromoted Pd/Al_2O_3 catalyst. And among the promoters used, monovalent ions enhance the hydrogenation activity to a greater extent as compared to divalent cations (when the activity is normalized for the extent of dispersion). And promoted catalysts show better stability compared to the unpromoted Pd/Al_2O_3. The net charge density at the metal site is responsible for phenol hydrogenation activity.

It was concluded that the alkali metal ions promote higher phenol hydrogenation activity while alkaline earth metal ions promote better thermal stability over palladium - alumina catalyst for the single step vapor phase hydrogenation of phenol to cyclohexanone

Narayanan, et al., (1998), Hydrotalcites (HTs) are prepared by low supersaturation and high supersaturation methods, containing CO_3^{2-} , Cl^-, SO_4^{2-} interlayer anions and with different Al(III)/Al(III)+Mg(II) (x.0.33 and 0.25) ratios. Palladium hydrotalcite catalysts are obtained by impregnation of $PdCl_2$ aqueous solution on HTs. Different precursors of palladium are used for loading the metal onto HT prepared at high supersaturation. HT and palladium HTs are well characterized by XRD, surface area, IR, SEM, DTA. CO chemisorption is used to estimate palladium dispersion and metal area. The activity is evaluated for phenol hydrogenation reaction

Uncalcined hydrotalcite was found to be good material for supporting palladium. The preparation method of hydrotalcite and the interlayer anions influence the dispersion and metal area of palladium in supported catalysts. HT1 prepared by the high supersaturation method and with interlayer CO_3^{2-} anion was found to be better among all the catalysts, in terms of metal dispersion and phenol hydrogenation activity. The anionic palladium precursors impregnated over these hydrotalcite supports help dispersion as well as activity towards phenol hydrogenation. The selectivity to cyclohexanone was always >90% over these catalysts, even when phenol conversion varied with available Pd area. Pd/HT was found to be a better catalyst than Pd/Al_2O_3 and Pd/MgO for phenol hydrogenation.

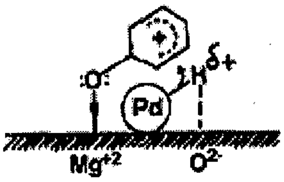
Scire, et al., (1998), The effect of the addition of calcium as promoter on the acid–base properties of the Pd/Al_2O_3 system has been studied by FT-IR of pyridine, pyrrole and CO adsorbed and by TPD of CO in order to better clarify the role of calcium on the performance of palladium supported catalysts in the selective hydrogenation of phenol to cyclohexanone.

The addition of calcium as promoter both poisons the Lewis acid sites of the alumina and causes a relevant increase in the number and the strength of basic sites (basic hydroxyl groups and . coordinatively unsaturated oxygen ions) of the Pd/Al_2O_3 system. A good correlation seems to exist between the surface acid–base properties and the catalytic performances of the Pd–Ca catalysts; the higher the basicity (or the lower the acidity) of the catalytic system, the higher the activity and the selectivity to cyclohexanone. The addition of calcium improves the performance of the monometallic Pd/Al_2O_3 sample by shifting the nature of the alumina support from acidic to basic. This modifies the adsorption–desorption equilibria of the reactant and favours the desorption of cyclohexanone. Moreover, it also causes a change in the interaction between the metal and the support, resulting in a higher electron density of Pd atoms.

Mahata, N., et al., (1997), Kinetics of vapor phase hydrogenation of phenol to cyclohexanone over Pd/MgO system has been studied in a flow microreactor under normal atmospheric pressure.

On the basis of kinetic results available on the hydrogenation of phenol over Pd/MgO, the rate-controlling step is a surface reaction between the strongly bound phenol molecule and the weakly adsorbed hydrogen atom. The higher value of *E*, observed ascribed to the absence of a facile migration or a spillover of hydrogen atom on the surface of magnesia.

The strength of adsorption of phenol depends upon the acid-base properties of the support. On magnesia, phenol in the form of phenolate is oriented with its aromatic ring non-planar with the surface. Based on information and results, a reaction mechanism is proposed wherein the strongly adsorbed phenol (as indicated by the negative order) in a non-planar form reacts with the dissociatively adsorbed hydrogen atom in a step-wise fashion to give cyclohexanone (Scheme 1).



Scheme 1

Scire, et al.,(1996) A detailed FT-IR investigation of CO, phenol and cyclohexanone adsorbed on alkali-doped Pd catalysts has been carried out in order to get information on the influence of the support and of the addition of promoters (alkali or alkaline earth metals) on the catalytic performance of Pd-supported catalysts in the selective hydrogenation of phenol.

On the basis of the PI'-IR results Phenol chemisorbs on the supports ($Al_2O_3$and MgO) in a phenolate form through the oxygen of phenolic O-H. IR data are not able to give information on the orientation of the phenol molecule. Only a small part of the chemisorbed phenol reacts with hydrogen leading to hydrogenation products. The reaction seems to occur between the phenol molecules chemisorbed on the support and located nearby the palladium particles and hydrogen activated on the metal. No long range spillover of hydrogen has been observed. The promoters, added in order to improve the catalytic performances of Pd catalysts, modify the electronic surroundings of palladium atoms but do not significantly change the chemisorption behaviour of the support.

Narayanan, et al., (1996), Hydrogenation of phenol was studied over Uncalcined and calcined hydrotalcite supported palladium catalysts and compared with the conventional γ-Al_2O_3 and MgO supported catalysts.

From the results it may be derived that hydrotalcite (HT), an anionic synthetic clay with basic properties may be a good material for supporting metals such as palladium. HT supported catalysts containing palladium (1-5 wt.-%) have been found to be very selective for phenol hydrogenation with a conversion of greater than 95%.

Kanta, R., et al., (1994), have presented single step hydrogenation of phenol over platinum alloyed with chromium; vanadium and zirconium on carbon support were investigated at atmospheric pressure and 200°C. They found that the alloying element shows a significant effect on the selectivities. As It was found that the Pt-(M=Cr, V and Zr) alloy catalysts are active for direct hydrogenation of phenol to cyclohexanone or cyclohexanol. A very high selectivity to cyclohexanone is obtained in single step on Pt-

Cr/C catalysts. Pt-Cr/C and Pt-V/C systems seemed to promising for single step vapor phase hydrogenation of phenol to cyclohexanone. On the other hand, Pt-Zr/C catalysts yield predominantly cyclohexanol.

Neri et al., (1993) have synthesized Palladium catalysts supported on Al_2O_3 and MgO. And used in the gas-phase hydrogenation of phenol to cyclohexanone. The results of the study showed that the catalytic properties of supported palladium catalysts are strongly influenced by the chemical composition of the catalyst. Basic oxide supports such as MgO, enhance the formation of cyclohexanone. With an acidic oxide such as Al_2O_3 cyclohexanone selectivity is lower. Moreover, the acidic sites of the support appear to be responsible for the deactivation of the catalytic system and for the formation of dicyclohexyl ether from cyclohexanol.

The catalytic properties of Pd/ Al_2O_3 can be improved by adding alkali metal components. The resulting catalysts have a better activity, selectivity to cyclohexanone and resistance to deactivation. The catalytic performance of the alkali-doped palladium catalysts can be attributed to a modification of the surface acid-base properties of the support. The support itself is responsible for the activation of the substrate towards the selective hydrogenation to cyclohexanone.

Narayanan, S., et al (1993), have prepared silica supported nickel catalysts using a homogeneous, controlled pH precipitation method.

Catalyst characteristics: Ni content 7-29 wt. %; surface area 304-352; dispersivity 40-91 %. Metal area 2.4-16 %. Hydrogenation experiments were carried out in a tubular down flow reactor on catalyst sample of 1.0 g. Motor driven syringe was used for feeding the pump at required rate. Cyclohexane was used as the solvent in 1:4 weight ratios.

Experimental conditions:

T=453° C, WHSV (mol $h^{-1}g^{-1}$) =0.013 and H/Phenol =19.6,

T=453° C, WHSV (mol $h^{-1}g^{-1}$) =0.027 and H/Phenol =9.8,

For the first set of conditions conversions ranged from 71-92 and selectivity of cyclohexanol varied from 79-90. And for the second set of conditions conversions ranged from 49-77 while selectivity of cyclohexanol varied from 65-82.

They have also studied the hydrogenation of aniline and benzene and found that irrespective of the functional groups attached to the aromatic ring, hydrogenation depends on the metal content available metal surface area.

Bhattacharya, K.G., et al., (1993) has studied the vapor phase hydrogenation of phenol over platinum and palladium supported on alumina and zeolite LTL in a vertical fixed bed high-pressure reactor. The major products of the hydrogenation reaction were cyclohexanone and cyclohexanol with cyclohexene and benzene as minor products.

It was concluded that the vapor phase hydrogenation of phenol seems very much dependent on the metal used. The conversion of phenol over platinum supported on alumina and zeolite LTL is more than twice (about 89% and 97% respectively) that compared to the respective palladium catalysts. (About 42% and 45% for alumina and zeolite supports, respectively) under same conditions of pressure and temperature for fresh catalysts.

The cyclohexanone/ cyclohexanol ratio is always lower in the case of the platinum catalysts than in the case of palladium catalysts under the same set of conditions. This work showed how differently two similar metals, palladium and platinum behave towards the hydrogenation of phenol. On the basis of percentage- d-character of the metallic bond (Pd: 46, Pt: 44). Low activity of palladium said to be limited by its ability to dissolve hydrogen, thus maintaining a low concentration of them on the surface. Platinum on the other hand, dissociates molecular hydrogen easily and has a larger concentration o f the hydrogen atom on the surface.

Itoh et al., (1993) have studied the vapor phase hydrogenation of phenol using a catalytic palladium membrane reactor (CPMR) at atmospheric pressure and in the temperature range 150-300^{0}. In this reactor phenol reacts with permeating hydrogen on the surface of the membranes. They tested four kinds of catalytic membranes made from palladium, $Pd_{93}Ni_7$, $Pd_{93}Ru_7$ and $Pd_{77}Ag_{23}$ were tested.

Experimental Results showed higher reactivity in the hydrogen permeating through the membranes compared to the pre-mixed in to phenol. The hydrogen permeability of the membranes decreased in the order of $Pd_{77}Ag_{23}$>Pd> $Pd_{93}Ru_7$> $Pd_{93}Ni_7$, whereas the hydrogenation activity of the membrane decreased in the order of Pd> $Pd_{93}Ni_7$> $Pd_{93}Ru_7$> $Pd_{77}Ag_{23}$. This showed that there is no particular relation between permeability and catalytic activity. Of the all membranes tested pure palladium showed the highest catalytic activity. Alloying of palladium with Ni, Ru and Ag considerably decreased the catalytic activity in the phenol hydrogenation.

With pure palladium membrane, a high phenol conversion of 90% and a high cyclohexanone selectivity of > 75% were reached. A temperature of 200° C was found to be necessary for the effective production of the cyclohexanone. They also found that the yield of cyclohexanone increased with increase in conversion of phenol until a conversion level o f approximately 0.9, after which it rapidly decreased due to the formation of cyclohexanol.

Kanta, R., et al., (1993) have studied the vapor phase hydrogenation of phenol using carbon supported platinum- chromium alloy. A 5-wt. % Pt loading on carbon was selected for alloying with chromium. The alloying of platinum with chromium resulted in 100% selectivity to cyclohexanone in hydrogenation of phenol while that on unalloyed platinum was about 84%. Also they observed that on Pt-Cr/C catalysts phenol directly hydrogenated to cyclohexanone and its further hydrogenation to cyclohexanol does not occur unlike in mono metallic platinum catalyst.

A part of improved selectivity of alloy catalysts ascribed to the dilution effect of the platinum sites. The isolation of active sites upon alloying produces a significant improvement in the dissipation of the heat of reaction resulting in high selectivity to cyclohexanone and the modifier may also selectively block the sites that would be responsible for the unselective hydrogenation.

Narayanan, et al., (1993) have studied two sets of supported nickel catalysts containing low (6-9) and high (42-58) on different supports. Weight percentages of metal are evaluated by hydrogen and oxygen adsorption measurements as well as by phenol hydrogenation. Metal area depends on crystallite size. They have found that there is dependence of phenol hydrogenation on hydrogen adsorption capacity of catalysts irrespective of the support type. And the product selectivity for cyclohexanol or cyclohexanone depends on H/Phenol mole ratio, and phenol feed rate or contact time.

CHAPTER 4

EXPERIMENTAL REVIEW

4.1. EXPERIMENTAL SET-UP

The experimental setup consists of an autoclave, PID controller, heating jacket, adjustable stirring regulator and hydrogen gas cylinder as shown in the Figure 4.1. Each of the equipment is discussed below.

4.1.1. Autoclave

The autoclave procured form the Parr Instruments Co. consisted of a vessel, head, tightening flanges and a teflon seal at the joining surfaces. The head was incorporated with following components and was shown in the Fig. 4.2.

1. A gas inlet valve for charging gas in to the reactor
2. A gas releasing valve for withdrawing gas or releasing pressure;
3. A dip tube connected to liquid sampling valve for withdrawing samples from the reactor under pressure;
4. A pressure gauge;
5. A safety rupture disc;
6. A thermocouple for temperature measurements;
7. A stirring shaft with attached impellers
8. A thermocouple sealed in a titanium sheath and attached to the bomb head to project directly in to the reactor cavity.

9. An internal cooling coil having a U-shape of continuous length of tubing

This high pressure reactor made of titanium can with stand pressures upto 2000 psi and 300°C temperature. The process conditions are maintained with the help of PID controller, heating jacket, thermocouple, magnetic drive and the cooling coil.

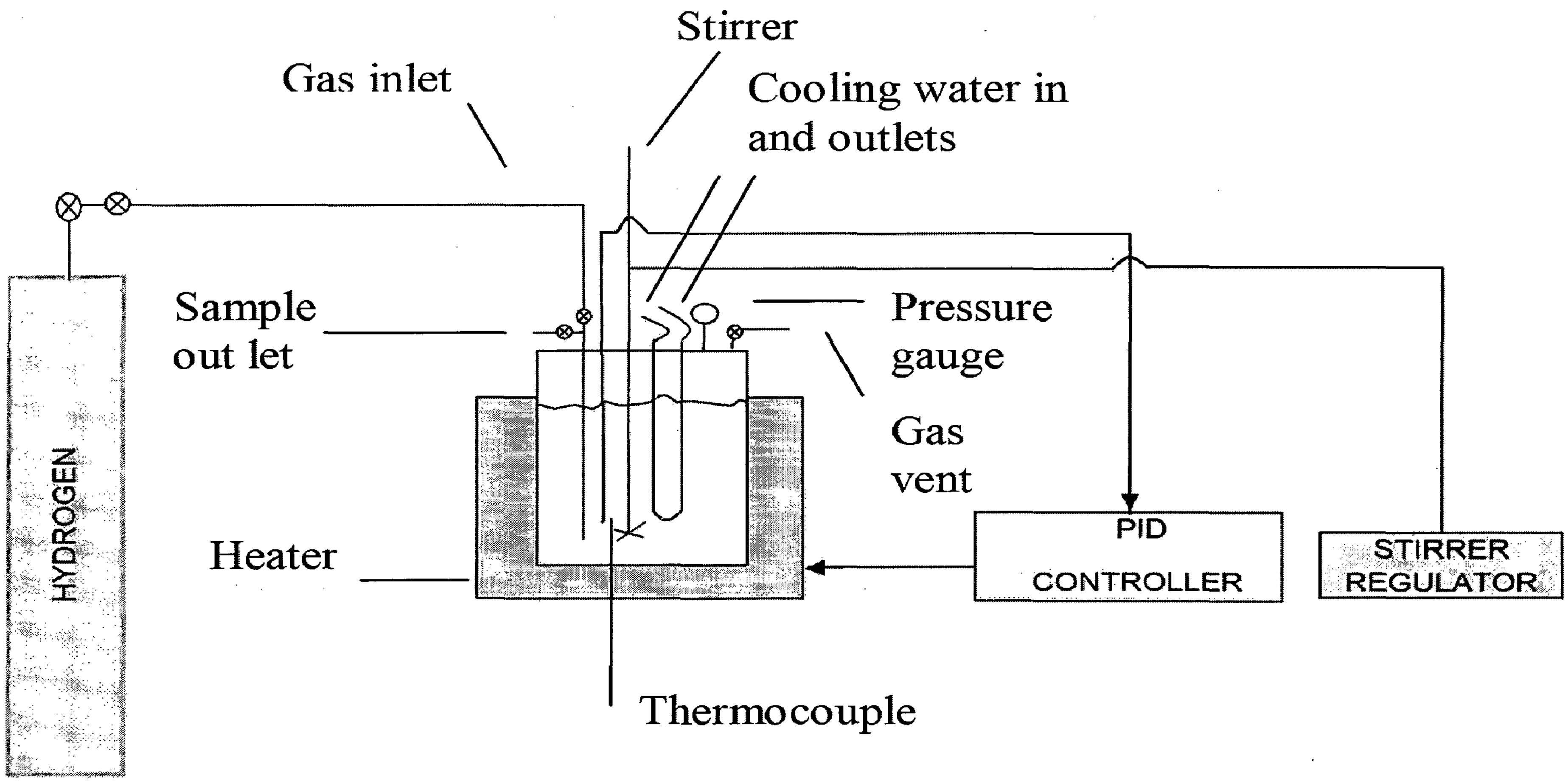


Figure 4.1. Schematic diagram of the experimental Set up.

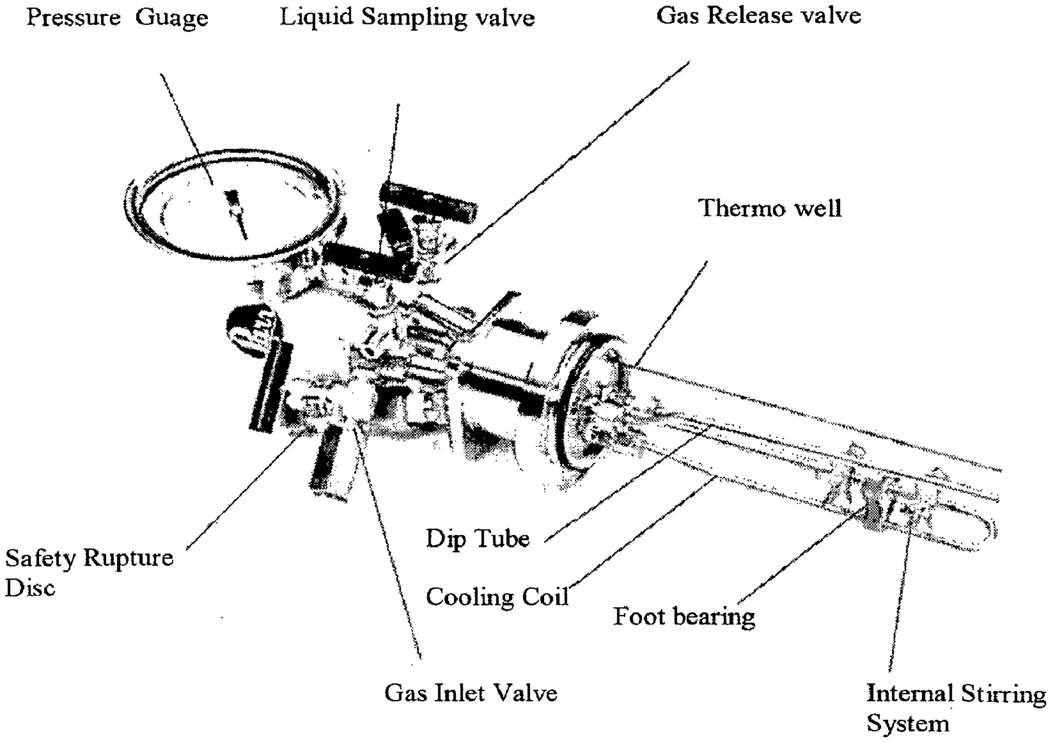


Figure 4.2. Head of the autoclave vessel

4.1.2. PID controller

The temperature was controlled with a PID controller whose parameters were tuned to the process equipment. The tuned PID control system measures the rate of approach to (or away from the) the set point and adjusts the proportional action to minimize the overshoot. An integral or reset function in the control compensates for offset produced by proportional control to ensure that the temperature will always match the set point. There is also derivative function in the PID system, which measures the rate of approach to or away from the set point and adjusts the proportional action to minimize temperature excursions above or below the established value.

4.1.3. The Heating Jacket

High temperature fabric mantle in aluminum shell has two options of low and high heating options. High heating reduces the time to reach the process set temperature while low heating is employed for the PID to control the small deviations.

4.1.4. Magnetic Drive

Magnetic drive is a stirrer drive system with a pack less magnetic drive to maintain a gas-tight seal on the rotating shaft. This also gives the better control of the string speed. For avoiding the high heat effects on the embedded magnets a small continuous flow of the water is maintained through the provided nozzles.

4.1.5. Internal Thermocouple

Reaction temperatures are measured with a Type J (iron-constantan) thermocouple installed in the reactor and used in conjunction with the PID controller

4.1.6. Cooling coil

An internal cooling coil having a U-shape of continuous length of tubing is installed in the reactor for required cooling needs; a slow, continuous flow of cold water through this provides the effective means for controlling temperature overshoots. The water flow was controlled manually.

4.1.7. Stirring Speed Regulator

Variable speed regulator is used for setting the stirrer speed and maintaining the desired agitation levels.

4.1.8. Gas Regulator

Hydrogen gas is fed to the reactor from the cylinder by using a two-stage pressure regulator.

4.1.9. Reactor Dimensions

Company	Parr Instruments`
Nominal size	450 ml
Maximum working capacity	325 ml
Inside diameter	2.05 inches
Inside depth	6.0
Impellers	4-blade

Table 4.1. Reactor dimensions

4.2. EXPERIMENTAL PROCEDURE

Hydrogenation was performed in a 450 ml titanium autoclave in slurry phase batch process. Temperature was controlled with a PID controller and high agitation was maintained with at stirrer high speed.

A known quantity of phenol dissolved in cyclohexane and desired amount of the catalyst were charged to the reactor vessel, tightened its head with split ring jaws. Keeping the reactor in the set up, the reactor was purged twice with hydrogen gas at low pressures. The PID controller was set to the required temperature and heating started. Agitation was also started and speed was set to the desired value. Pressure of hydrogen gas was kept lower than the desired level to give allowance for pressure increase with heating. When the temperature of the vessel reached the required temperature, hydrogen gas was fed to the desired pressure. Thus the PID controller maintains the temperature at the desired level. Hydrogen gas was fed manually for every small drop of pressure in the reactor due to the consumption in the reaction, thus pressure was maintained at ± 1/2 bar of the desired pressure.

The time at which the reactor temperature reaches the set point was taken as the reaction start temperature. To monitor the progress of the reaction, small amount of the reaction mixture samples (2-3 ml) were withdrawn from the sampling valve at different time intervals. In order to avoid the catalyst particles coming along the sample, stirrer was stopped a minute before the sample was withdrawn.

The samples were analyzed by Gas Chromatography. The reaction was continued to the desired time. After the completion of the reaction the reactor was cooled to room temperature. Hydrogen gas was released slowly to the atmosphere. The reactor reaction mixture was filtered to separate the catalyst, the reaction products were separated by simple distillation.

4.3. GAS CHROMATOGRAPHY

The separation of simple and complex mixtures into their components, as well as the isolation of the individual components, has become an important physical method of separation in all branches of chemistry. One important physical method of separation and isolation is liquid gas chromatography.

A Gas chromatograph or Gas liquid chromatograph is a chemical analysis instrument for separating and identifying chemicals in a sample. It is based on the principle of adsorption technology, in which liquid is a still media on which moving gas having different component is adsorbed. Heart of the gas chromatograph system is the separation column. The function of the column is to separate and concentrate different components in order to maximize the detection signal. Generally gas chromatograph consists of following components

1. Carrier gas and apparatus for its control and measurement.
2. A column and a temperature controlled environment.
3. Injection port and a system for the introduction of the sample into the column (Micro syringe).
4. Column oven
5. Detector (Flame ionization (FID) general purpose - modest sensitivity)
6. A recorder or any output device

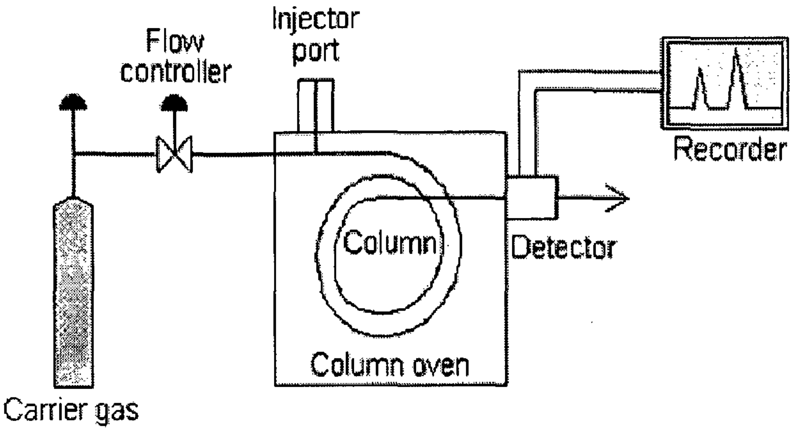


Figure 4.3. Descriptive diagram of a chromatograph

4.3.1. Carrier Gas

The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas was often dependant upon the type of detector which used. The carrier gas system also contains a molecular sieve to remove water and other impurities. Valves and pressure gauge were used to control and measure the flow of the gas.

4.3.2. Packed Column

Packed columns contains a finely divided, inert, solid support material (eg. diatomaceous earth) coated with a liquid or solid stationary phase. The nature of the coating material was to determine what type of materials will be most strongly adsorbed. Thus numerous columns were available that were designed to separate specific types of compounds. Most packed columns are 1.5 - 10m in length and have an internal diameter of 2 - 4mm. The outer tubing is usually made of stainless steel or glass.

4.3.3. Column temperature

For precise work, column temperature must be controlled to within tenths of a degree. The optimum column temperature was dependant upon the boiling point of the sample. As a rule of thumb, a temperature slightly above the average boiling point of the sample was maintained and the samples will be eluted within time of 2 - 30 minutes. Minimal temperatures give good resolution, but increase elution times. If a sample has a wide boiling range, then temperature programming can be useful. The column temperature was increased (either continuously or in steps) as separation proceeds.

4.3.4. Sample injection port and system for sample introduction

For optimum column efficiency, the sample should not be too large, and should be introduced onto the column as a "plug" of vapour - slow injection of large samples causes band broadening and loss of resolution. The most common injection method is by a micro syringe which is used to inject sample through a rubber septum into a flash vaporizer port at the head of the column. The temperature of the sample port is usually about 50^0 C higher than the boiling point of the least volatile component of the sample. For packed columns, sample size ranges from tenths of a microlitre up to 20 microlitre.

The injector can be used in one of two modes; split or splitless. The injector contains a heated chamber containing a glass liner into which the sample is injected through the septum. The sample vapourises to form a mixture of carrier gas, vapourised solvent and vapourised solutes. This mixture passes onto the column, but most exits through the split outlet. The septum purge outlet prevents septum bleed components from entering the column.

4.3.5. Detectors

There are many detectors which can be used in gas chromatography. Different detectors will give different types of selectivity. A *non-selective* detector responds to all compounds except the carrier gas, a *selective detector* responds to a range of compounds with a common physical or chemical property and a *specific detector* responds to a single chemical compound. Detectors can also be grouped into *concentration dependant detectors* and *mass flow dependant detectors*. The signal from a concentration dependant detector is related to the concentration of solute in the detector, and does not usually destroy the sample. Dilution of with make-up gas will lower the detectors response. Mass flow dependant detectors usually destroy the sample, and the signal is related to the rate at which solute molecules enter the detector. The response of a mass flow dependant detector is unaffected by make-up gas. The detector used for the sample analysis is a Flame ionization detector.

4.3.5.1. Flame ionization detector

The effluent from the column is mixed with hydrogen and air, and ignited. Organic compounds burning in the flame produce ions and electrons which can conduct electricity through the flame. A large electrical potential is applied at the burner tip, and a collector electrode is located above the flame. The current resulting from the pyrolysis of any organic compounds is measured. FIDs are mass sensitive rather than concentration sensitive; this gives the advantage that changes in mobile phase flow rate do not affect the detector's response. The FID is a useful general detector for the analysis of organic compounds, it has high sensitivity, a large linear response range, and low noise. It is also robust and easy to use, but unfortunately, it destroys the sample.

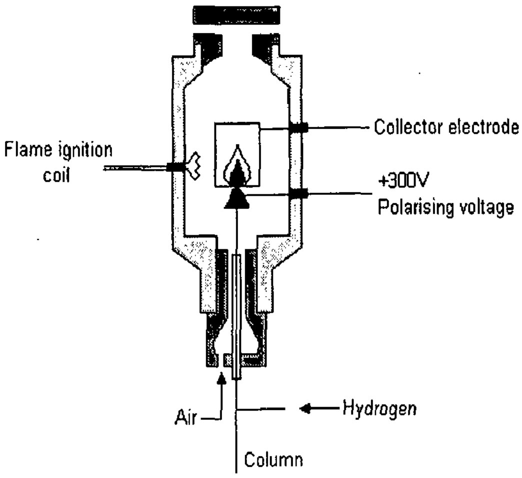


Fig. 4.4. Descriptive diagram of Flame Ionization Detector

4.3.6. Qualitative analysis using the column

Different substances take different lengths of time to eluted from the instrument (reach the detector). The retention time is the time between when the sample was injected and the time of the highest part of a peak emerging (being detected by the detector).

A recorder will automatically print out retention times and percent area under the curve. The percent area is relative to the amounts of each chemical in the sample. Unknown graph is then compared to the known samples to determine what is there in the unknown.

CHAPTER 5

EXPERIMENTAL RESULTS AND DISCUSSION

5.1. REACTION COMPONENTS

Experiments were conducted to study the influence of Palladium catalyst on the conversion, selectivity of liquid phase hydrogenation of phenol. Following were the components used in the experiments.

5.1.1. Phenol

Each of the experiment was conducted with same initial concentration of phenol of 10 g. in 150 ml of solvent. That is an initial molar concentration of 0.70839 mol/l was taken for all the experiments

5.1.2. Solvent

Considering hydrogen and phenol solubility levels in different solvents, cyclohexane was used as solvent for all the experiments. Saturation solubility of hydrogen in cyclohexane is 3.97×10^{-3}(mol/liter). Cyclohexane was used in all the experiments.

5.1.3 Catalyst

Commercial catalysts 5%Pd/C and 2% Pd/C, form Arora Matthey Ltd, were used for the experiments.

5.1.4. Hydrogen

Pure hydrogen gas of 99.8% was used for all the experiments conducted.

5.2 EXPERIMENTAL CONDITIONS

The reaction system is a rather complex, as there are three phases present and several mass transfer steps involved. The mass transport steps are (i) Hydrogen diffusion within the gas phase,(ii) hydrogen gas-liquid film diffusion at the interfaces, (iii) hydrogen and phenol liquid-solid film diffusion around the catalyst particle, and (iv) hydrogen and phenol diffusion within the particle.

In order to carry out kinetic studies under conditions such that the mass transfer and other complex effects are absent, an agitated slurry reactor was used for maintaining these conditions.

Step (i) can be neglected in this case, because hydrogenations were carried out with almost pure gaseous hydrogen.

Stirring of the reaction mixture keeps the catalyst suspended and disperses the hydrogen gas in the liquid phase. Increasing stirring speed is known to increase gas-liquid interfacial area, there by increasing the rate of mass transfer in steps (ii) and (iii). Thus external mass transfer resistance was minimized by employing high agitation levels. Agitator was kept at 1200 rpm to achieve this for all the experiments.

Catalyst particle size affects step (iv). The lower the particle size, the higher the rate of mass transfer hence small catalyst particles were used to minimize the intraparticle concentration gradients.

5.3. ASSUMPTIONS

1. Concentrations of the all the reactants and products is constant through out the reactor at any time.

2. Constant pressure of 20 bars is assumed for the all experiments.
3. Isothermal conditions were assumed leaving the small fluctuations in the temperature.
4. Saturation solubility of hydrogen in Cyclohexane is 3.97×10^{-3}(mol/liter) does not vary much with the temperature, and is considered remains constant through the reaction time
5. Intraparticle diffusional resistance is negligible.

5.4. EXPERIMENTS

Experimental runs were done at different temperatures and with varying catalyst weights and contents to study their effect on the selectivity and activity of the liquid phase hydrogenation of phenol using carbon supported palladium catalysts.

Table 5.1 shows the temperature, pressure, catalyst and metal content employed for the each experiment conducted.

5.5. EXPERIMENTAL RESULTS

For each of the experiment, mass fraction profiles of the reaction mixtures with respect to time, were given in Figures 5.1 -5.7.

Selectivity to cyclohexanone measured as the ratio of moles of cyclohexanone formed by the total moles of cyclohexanone and cyclohexanol and benzene formed at the highest cyclohexanone concentration. Selectivitties thus obtained were given in the Table 5.2.

EXPT NO	PHENOL WT (g.)	SOLVENT	AMOUNT OF SOLVENT (ml)	CATALYST	AMOUNT OF CATALYST (g.)	TEMPERATURE (^{O}C)	PRESSURE (bar)
1	10	CYCLOHEXANE	150	5%Pd/C	0.5	125	20
2	10	CYCLOHEXANE	150	5%Pd/C	0.5	150	20
3	10	CYCLOHEXANE	150	5%Pd/C	0.5	175	20
4	10	CYCLOHEXANE	150	5%Pd/C	0.3	125	20
5	10	CYCLOHEXANE	150	5%Pd/C	0.3	150	20
6	10	CYCLOHEXANE	150	5%Pd/C	0.3	175	20
7	10	CYCLOHEXANE	150	2%Pd/C	0.3	150	20

Table 5.1 Experimental conditions

5.5.1 At 125°C, 20 bar with 0.5g. of 5%Pd/C

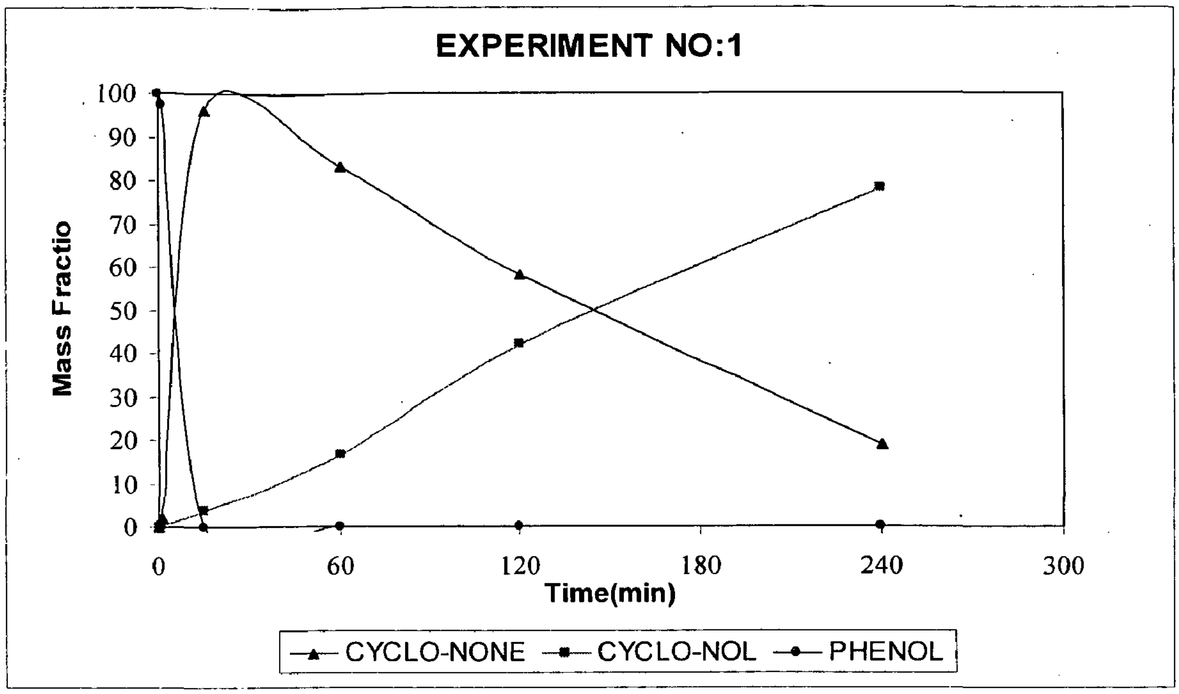


Figure 5.1 Mass fraction profiles of the reaction mixture for experiment no 1

5.5.2 At 150°C, 20 bar with 0.5g. of 5%Pd/C

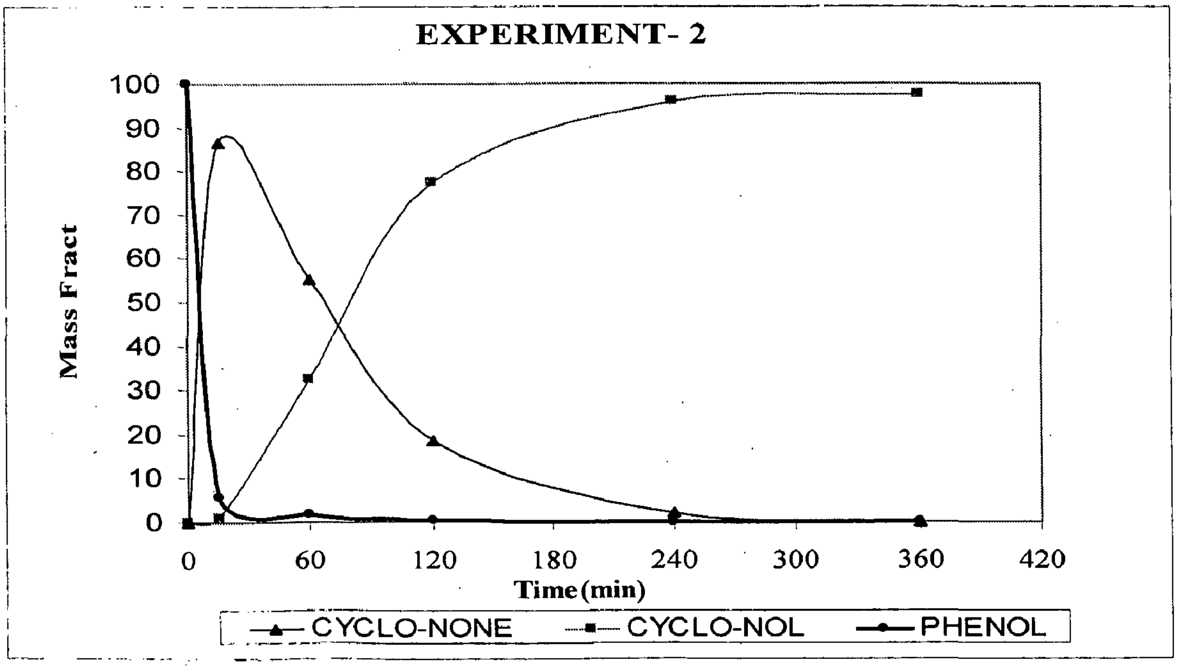


Figure 5.2 Mass fraction profiles of the reaction mixture for experiment no 2

5.5.3 At 175°C, 20 bar with 0.5g. of 5%Pd/C

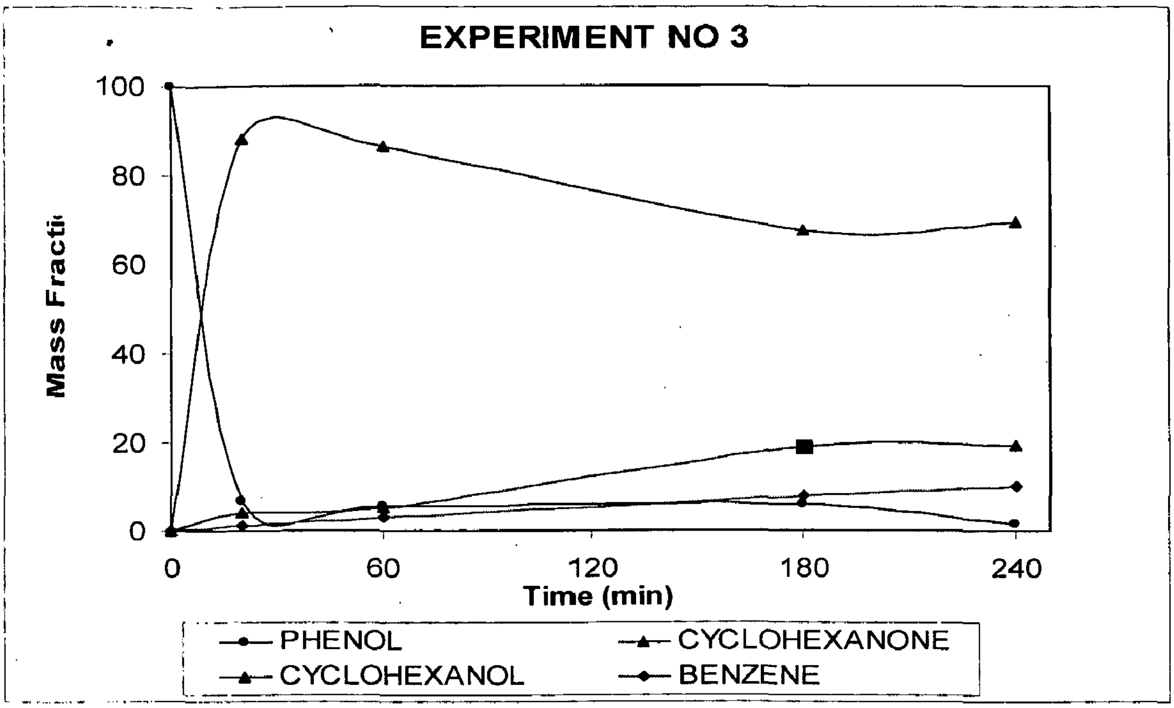


Figure 5.3 Mass fraction profiles of the reaction mixture for experiment no 3

5.5.4 At 125°C, 20 bar with 0.3 g. of 5%Pd/C

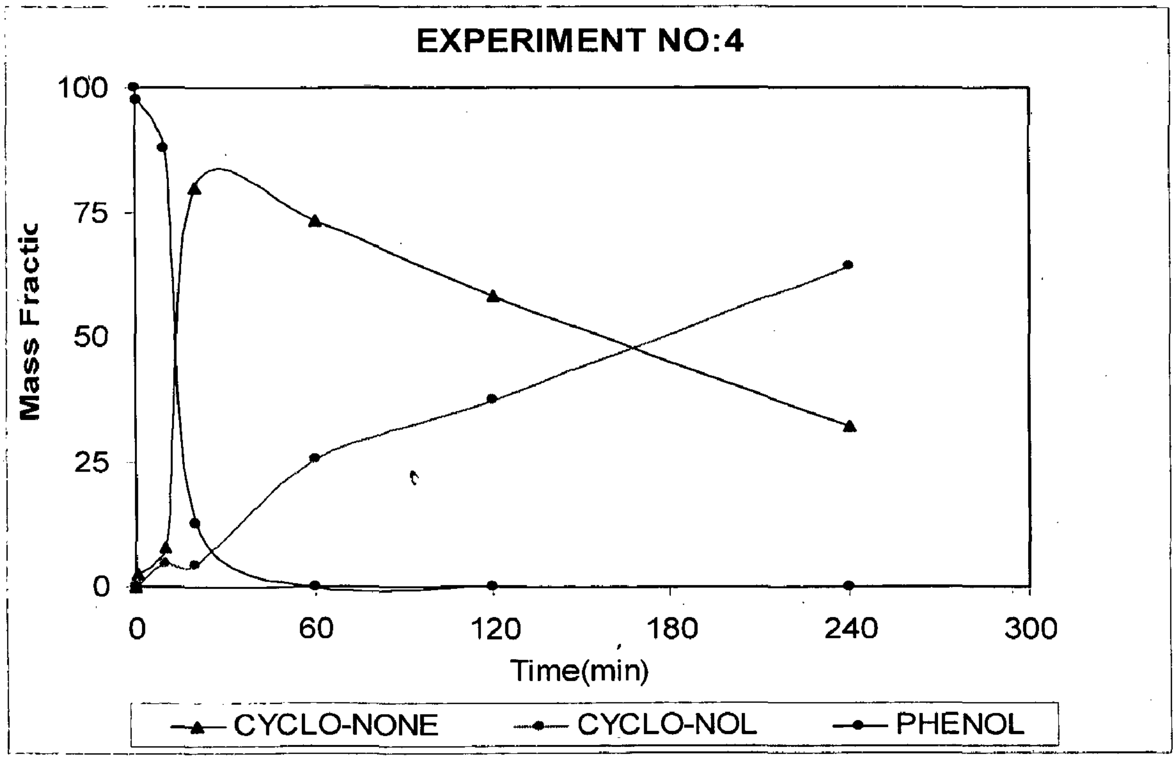


Figure 5.4 Mass fraction profiles of the reaction mixture for experiment no 4

5.5.5 At 150°C, 20 bar with 0.3 g. of 5%Pd/C

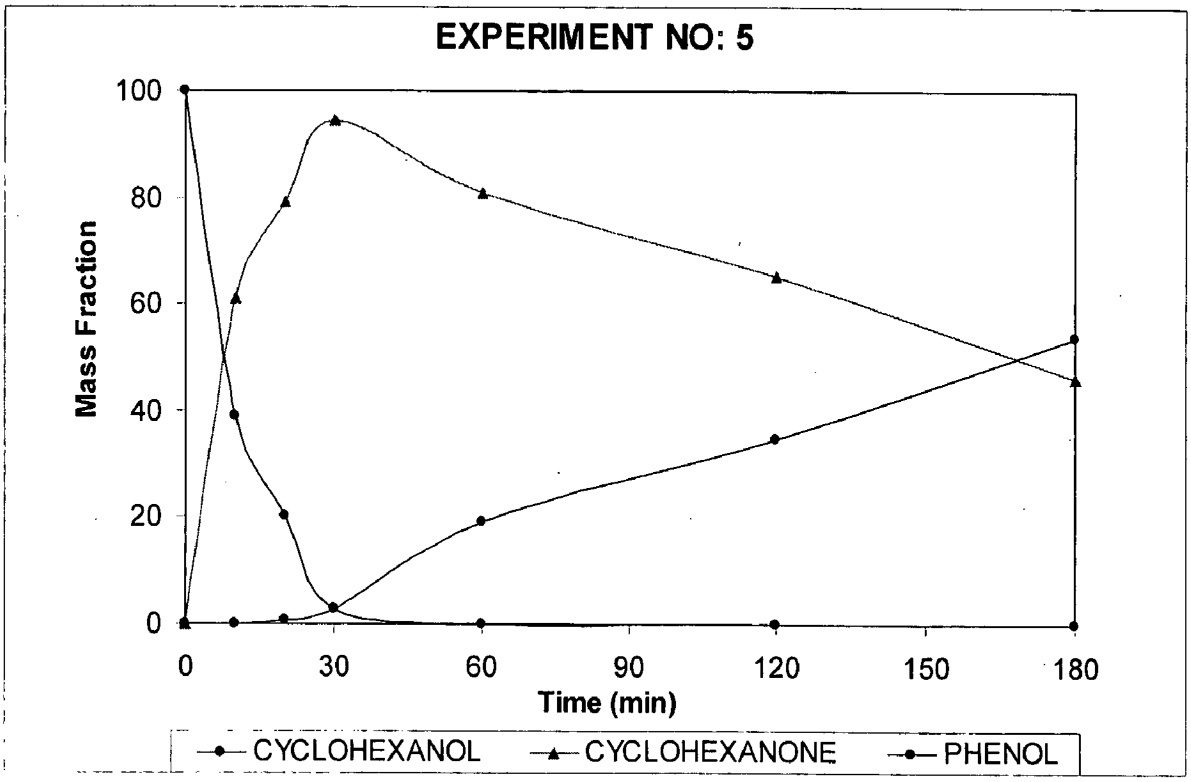


Figure 5.5 Mass fraction profiles of the reaction mixture for experiment no 5

5.5.6 At 175°C, 20 bar with 0.3 g. of 5%Pd/C

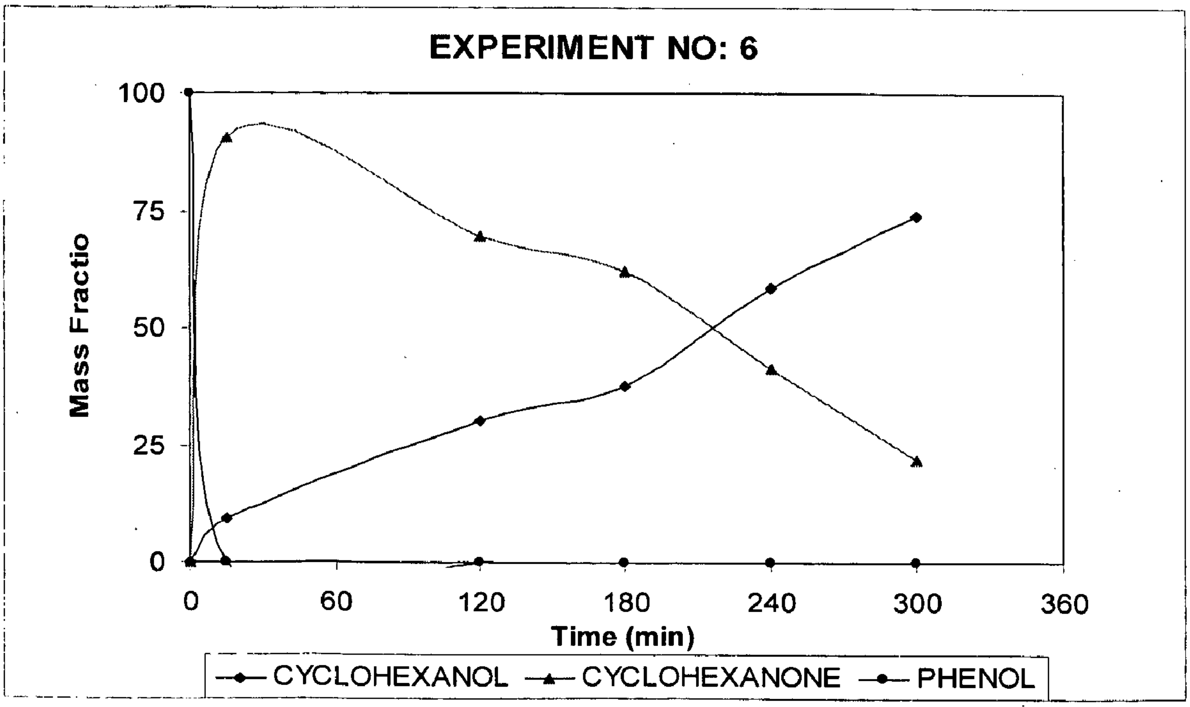


Figure 5.6 Mass fraction profiles of the reaction mixture for experiment no 6

5.5.7 At 175°C, 20 bar with 0.3 g. of 2%Pd/C

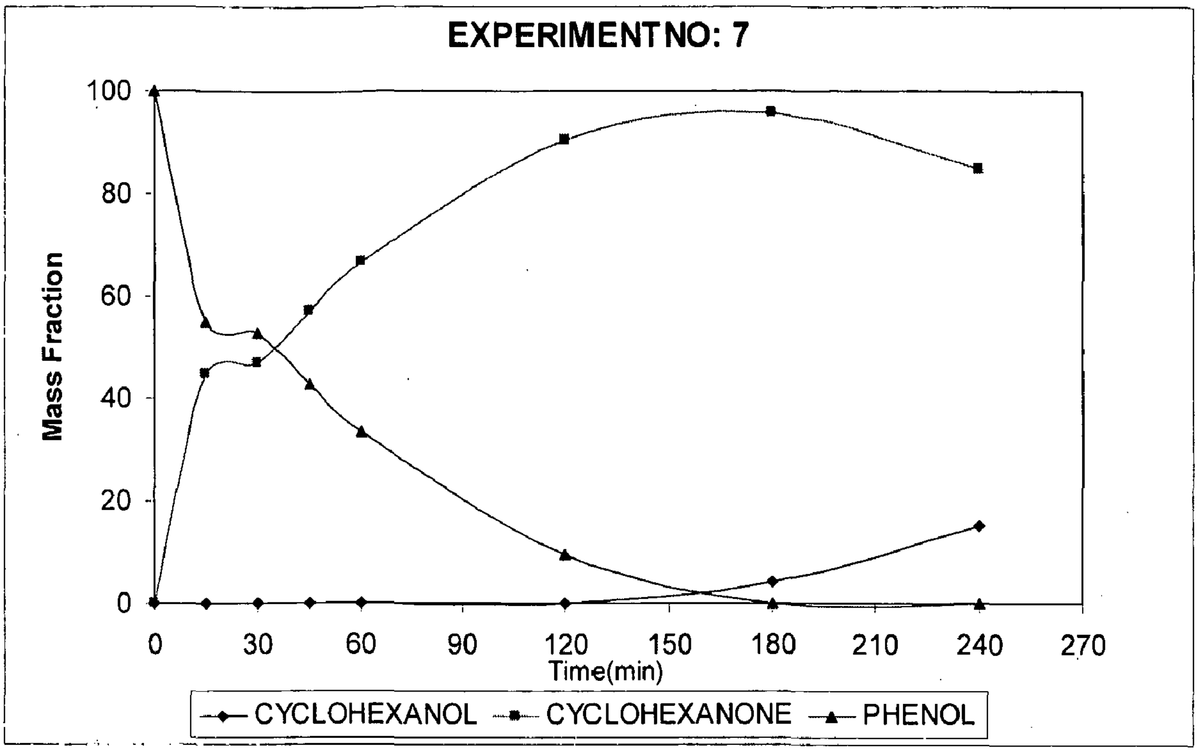


Figure 5.7 Mass fraction profiles of the reaction mixture for experiment no 7

Experiment nol	Catalyst	Wt of the catalyst (g.)	Temperature	Selectivity (mol/mol)
1	5% Pd/C	0.5	125	0.96166
2	5% Pd/C	0.5	150	0.9871
3	5% Pd/C	0.5	175	0.94255
4	5% Pd/C	0.3	125	0.9496
5	5% Pd/C	0.3	150	0.97133
6	5% Pd/C	0.3	175	0.9095
7	2% Pd/C	0.3	150	0.960

Table 5.2 Cyclohexanone selectivities obtained in the experiments

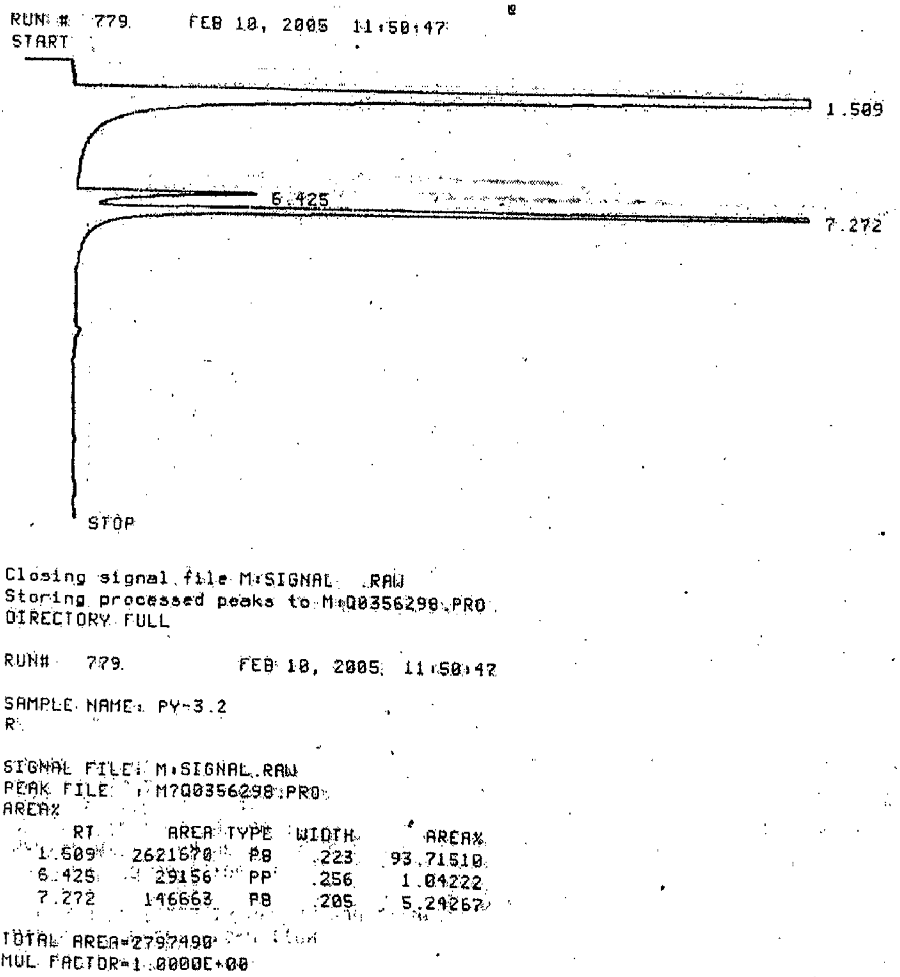
5.6 CALCULATION OF PHENOL CONSUMPTION RATE

Mass percentage analysis reports of the each of the sample were converted to molar concentrations, to determine the initial rate of reaction of phenol at zero time.

5.6.1. Sample Calculations

Sample calculation for converting mass percentage from the GC analysis, to molar concentrations:

For the 60 minute sample of the experiment 1, GC analysis report is shown in the Figure.5.8; data from the report is taken given in table 5.3. The mass percentage data was converted to molar concentrations by following manner.



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RUN #  779.      FEB 10, 2005  11:50:47
START

 STOP

Closing signal file M:SIGNAL  .RAW
Storing processed peaks to M:Q0356298.PRO
DIRECTORY FULL

RUN#   779.          FEB 10, 2005  11:50:42

SAMPLE NAME: PY-3.2
R

SIGNAL FILE: M:SIGNAL.RAW
PEAK FILE   : M?Q0356298.PRO
AREA%
     RT       AREA TYPE  WIDTH      AREA%
   1.509   2621670  PB    .223   93.71510
   6.425     29156  PP    .256    1.04222
   7.272    146663  PB    .205    5.24267

TOTAL AREA=2797490
MUL FACTOR=1.0000E+00
```

Figure 5.8. GC analysis Report of the sample

COMPONENT	RT	AREA	WT %
PHENOL	ABSENT	0	0
CYCLOHEXANOL	6.425	29156	1.04222
CYCLOHEXANONE	7.272	146663	5.242666
CYCLOHEXANE	1.509	2621670	93.71511

Table 5.3 Data from the GC analysis of the sample

Density of cyclohexane = 0.778 gm/cc= 778 gm/litre.

Volume of cyclohexane present in 100 gm of sample is

= Wt. % of cyclohexane/ Density of cyclohexane

$$= \frac{93.7151138}{778}$$

= 0.120456 litres.

In the unit sample no of moles of phenol present

= Wt. % of phenol/Mol wt. of phenol.

= 0/94.11= 0 g. moles.

In the unit sample no of moles of cyclohexanol present

= Wt. % of cyclohexanol/Mol wt. of cyclohexanol.

$$= \frac{1.04222}{100.16}$$

= 0.010406

In the unit sample no of moles of cyclohexanone present

= Wt. % of cyclohexanone/Mol wt. of cyclohexanone

$$= \frac{5.2426658}{98.16}$$

= 0.053409

Molar concentration of phenol = no. of moles of phenol/litre solvent

$$= \frac{0}{0.120456}$$

= 0 g. moles/ litre.

Molar concentration of cyclohexanol

= no. of moles of cyclohexanol/litre solvent

$$= \frac{0.010406}{0.120456}$$

= 0.086384694 g. moles/litre.

Molar concentration of cyclohexanone

= no. of moles of cyclohexanone/litre solvent

$$= \frac{0.053409}{0.120456}$$

= 0.443393365 g. moles/litre.

5.6.2 Activity

Activity was obtained by the derivation of the curves concentration *vs* time for phenol, cyclohexanone and cyclohexanol at zero time, and has been expressed as initial reaction rates. These initial rates were denoted as $-r_{ph}, r_{none}$ *and* r_{nol} for phenol, cyclohexanone and cyclohexanol respectively.

5.6.3 Derivation of the curves

Curve fitting of the experimental data curves have been derived with MICROSOFT EXCEL. Some of the polynomials, which were fitted well with the data, only for limited required range, were also considered.

Concentration profiles of the reaction mixture at different time intervals from the GC analysis were given in the table 5.4, below.

TIME(min)	PHENOL	CYCLOHEXANOL	CYCLOHEXANONE
0	0.70839	0	0
10	0.298	0.0095	0.252
15	0	0.019670172	0.493473005
30	0	0.04	0.47
60	0	0.086384694	0.443393365
120	0	0.223595229	0.315041517
240	0	0.413625575	0.101882296

Table 5.4. Concentration, time data of the experiment no: 1

The data of the concentration variation of the phenol, and cyclohexanone and cyclohexanol with time were shown in the Figure 5.2. Activity, selectivity was obtained by the derivation of the curves concentration *vs.* time.

Polynomial of phenol concentration vs. time curve:

$$C_{ph} = -0.0012t^2 - 0.0287t + 0.7084 \qquad (5.1)$$

Polynomial for cyclohexanone concentration vs. time curve:

$$C_{none} = 0.0015t^2 + 0.0098t \qquad (5.2)$$

Polynomial for cyclohexanol concentration vs. time curve:

$$C_{nol} = 2x10^{-07}t^2 + 0.0017t \qquad (5.3)$$

At zero time:

Initial reaction rate of phenol $(-r_{ph}) = 0.0287$

Initial reaction rate of cyclohexanone $(r_{one}) = 0.0098$

Initial reaction rate of cyclohexanol $(r_{nol}) = 0.001$

Similarly initial rates were found for the all the experiments and as shown in the Table

EXPT NO	CATALYST	AMOUNT OF CATALYST (g.)	TEMPERATURE (^{0}C)	PRESSURE (bar)	$-r_{ph}$ (mol/ L min)
1	5%Pd/C	0.5	125	20	0.0287
2	5%Pd/C	0.5	150	20	0.0696
3	5%Pd/C	0.5	175	20	0.0820
4	5%Pd/C	0.3	125	20	0.0438
5	5%Pd/C	0.3	150	20	0.032
6	5%Pd/C	0.3	175	20	0.0283
7	2%Pd/C	0.3	150	20	0.005

Table 5.5.Experimental results, showing initial rates of phenol conversion

5.6.4 Apparent activation energy

Apparent activation energy was determined from the slope of $\ln(-r_{ph})$ *vs* 1/T line, taking $-r_{ph}$ in mol/l/hr and Temperature in ^{O}K. And the activation energy was found to be 31.51 kJ/mol.

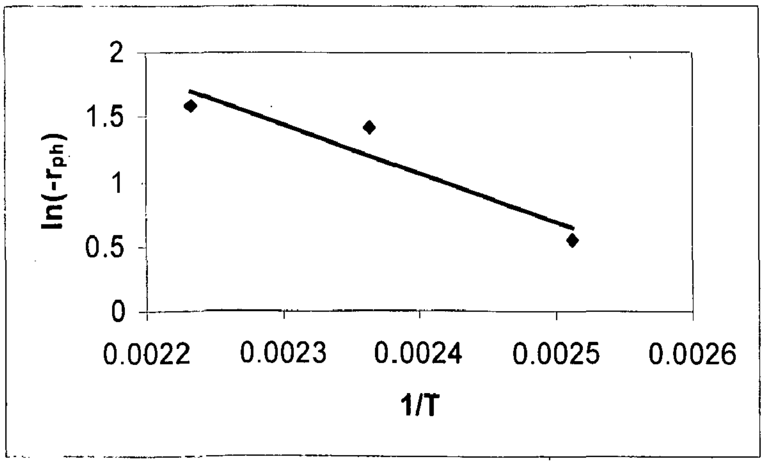

Figure 5.9. Effect of temperature on the consumption rate (mol/litre/hr) of phenol, from experiments 1,2 and 3.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

Experimental study of Liquid phase catalytic hydrogenation of phenol was carried out to study the selectivity conversion and phenol consumption rate.

From the experiments it is observed that only products formed by hydrogenation of phenol using carbon supported catalyst are cyclohexanone and cyclohexanol. It is also observed that phenol was completely converted within the first one hour of the reaction time, for experiments 1-6.

It is also observed that at the beginning of the reaction there is no formation of cyclohexanol, until some cyclohexanone was formed. This implies palladium hydrogenates phenol to cyclohexanone and but not to cyclohexanol, although cyclohexanol is also hydrogenated to cyclohexanol in a consecutive reaction with the former.

6.1.1 Effect Of Temperature

Results from the experiments 1, 2 and 3 showed an increase in initial phenol consumption rate with the temperature. Apparent activation energy of phenol consumption was calculated from the slope of of $\ln(-r_{ph})$ *vs* 1/T line, and found to be 31.51 kJ/mol.

High selectivity of 0.9871mol/mol was observed at an intermediate temperature of 150°C, while at 125 and 175 showed 0.96166 and 0. 94255 respectively.

6.1.2 Effect Of The Catalyst Load

From the experiments 2, 3,5 and 6 it can be observed that an increase of 2/3 in the catalyst load will increase the initial reaction rate to 2-3 times.

6.1.3 Effect Of Metal Content

From the experimental results of 5 and 7, it can be deduced that, though there is no much difference in the selectivity, with decrease in metal content reaction rate also decreases rapidly.

6.2 RECOMMENDATIONS FOR FUTURE WORK

There many aspects which are to be studied in order to ascertain the complete rate kinetics the carbon supported palladium catalyzed hydrogenation of phenol. Following are the recommendations for the future study.

1. Effect of hydrogen partial pressure on reaction rate and selectivity.
2. Determination of the mass transfer resistances and how they effect the selectivity and conversion. From these studies kinetic regime can also be ensured.
3. Characterization of the catalyst in order to find the exact nature of the catalyst which in turn helps in estimating the mass transfer resistances. Characterization also helps in regeneration of the catalyst.
4. An increase in the initial concentration of the phenol is also recommended for the better understanding of the system.

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