Chapter II

Experimental and characterization techniques
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2.1. Materials:
Nitrobenzene, aniline, polyvinylpyrrolidone, formaldehyde, sodium hydroxide, ethanol, HCl, dimethyl sulfoxide were purchased from S.d. fine chemicals, India. Methanol (HPLC), methanol (LR), 2-butyne-1,4-diol, and charcoal were obtained from Merck, India. $p$-Aminophenol, Ni(NO$_3$)$_2$, PtCl$_4$, PdCl$_2$, 4-chloronitrobenzene, 2-chloronitrobenzene, 3-chloronitrobenzene, 2-chloroaniline, 3-chloroaniline, 4-chloroaniline, phenylacetylene, ethylbenzene, styrene, 2-butene-1,4-diol and butane-1,4-diol were purchased from Sigma-Aldrich, Bangalore, India. Distilled water was deionized by using Millipore (Mili-Q) water system. High purity grade nitrogen and hydrogen cylinders used for the hydrogenation reactions were procured from M/s. Inox Ltd. Mumbai.

2.2. Catalyst preparation:
Various catalysts were used for hydrogenation reactions and the details of catalyst preparation are given below. A schematic of the experimental setup used for the catalyst preparation is shown in Figure 2.1.

![General setup for catalyst preparation](image)

Figure 2.1. General setup for catalyst preparation
2.2.1. 1% Pt/CaCO\(_3\) catalyst:
For the preparation of 1%Pt/CaCO\(_3\) catalyst, 0.166 g of PtCl\(_4\) was completely dissolved in minimum amount of water by adding a small quantity of HCl. Under stirring, already prepared slurry of 10 g CaCO\(_3\) was added to the above solution and temperature was maintained at 353 K. After 1h, formaldehyde was also added under stirring. Then the reaction mixture was cooled, filtered to obtain the catalyst, which was then dried at room temperature under vacuum. The powdered catalyst was then pelletized in the form of pellets of 4-mm diameter to be used in the fixed bed reactor for the hydrogenation of 2-butyne-1,4-diol.

2.2.2. 1% Pt/C catalyst:
For the purpose of preparing Pt/C catalyst first, the charcoal support was activated by an acid treatment. In a typical procedure, 10 g of charcoal was refluxed with 100 mL 10% HNO\(_3\) for 6 h, under magnetic stirring. After filtration through Whatman filter paper, it was then washed several times with distilled water till the pH of the filtrate became ~7. This activated charcoal was then dried in an oven for 12 h, at 373 K.
For the preparation of 1% Pt/C catalyst, 0.053 g of H\(_2\)PtCl\(_4\).6H\(_2\)O was completely dissolved in minimum amount of water. Under stirring, already prepared slurry of 2 g activated carbon was added to the above solution, and the temperature was maintained at 353 K. After stirring for 1 h, formaldehyde was added. Then the reaction mixture was cooled to room temperature and then filtered to obtain 1% Pt/C catalyst which was dried at room temperature under vacuum. Similarly 2, 3 and 5% Pt supported on carbon catalysts were prepared using the procedure described above.

2.2.3. Supported bulk Pd catalyst:
For the preparation of 0.25 % Pd/C catalyst, 0.0083 g of PdCl\(_2\) was completely dissolved in minimum amount of water. Under stirring, already prepared slurry of 2 g carbon was added to the above solution and the temperature was maintained to 353 K. After stirring for 1 h, formaldehyde was added. Then the reaction mixture was cooled to room temperature and then filtered to obtain the reduced catalyst. After the filtration, catalyst
was dried at room temperature under vacuum. Similarly, Pd catalyst supported on alumina, silica and calcium carbonate were prepared.

2.2.4. Colloidal Pd catalyst:

0.343 g of polymer polyvinylpyrrolidone (PVP) was added to 15 ml of H₂PdCl₄ solution (prepared by addition of 0.0083 g of PdCl₂ to a mixture of 13 ml of water and 2 mL of 0.2M HCl). To this solution, 30 mL of mixture of ethanol:water (30:70) was added. The initial pH of the solution was found to be 3 which was adjusted to pH 7 by adding slowly 10% (w/w) NaOH. This solution was diluted to 100 mL by adding a mixture of ethanol:water and refluxed in a 250 mL flask at 353 K for 3 h. After 3 h, the color changed to dark brown to form polymer protected Pd nanoparticles.

2.2.5. Supported nano Pd catalyst:

First the colloidal Pd catalyst was prepared as per the procedure given in section 2.2.4. For depositing the colloidal Pd on to the support, activated carbon (2 g) was added to the above solution under stirring for 16 h, after which the solid catalyst was separated by filtration. In a similar way, Pd nanoparticles supported on alumina, silica and calcium carbonate were prepared.

2.2.6. Pd supported on CNT catalyst:

In order to prepare Pd/CNT catalyst, first the multiwalled CNTs were grown on MgO-supported, Fe-Mo powder catalyst by thermal decomposition of methane in a quartz tubular furnace (Firstnano-ET2000, USA). Typically, 100 mg of the catalyst on a quartz plate was placed into the center of the quartz tube and furnace was heated to 1223 K in an argon flow of 1000 sccm. The reaction began as Ar was replaced by a mixture of CH₄ (1000 sccm) and H₂ (200 sccm). After 30 minutes, the flow was switched to Ar again to cool the furnace to ambient temperature. The synthesized CNTs were purified by acid treatment with 3-4 N aqueous solution of HNO₃. Further the CNTs were magnetically stirred at room temperature for 6 h, filtered through Whatman 200 nm, 47 mm diameter PTFE membrane and then washed several times with de-ionized water till the pH reached close to 7. The purified sample of CNTs was then dried in air at room temperature. The
sample was then heated at 773 K in H₂ atmosphere to remove the amorphous carbon and graphitic nanoparticles. The purified CNTs were treated with a mixture of HNO₃ and H₂SO₄ at 353 K for a period of 24 h. The acid treated CNTs were again filtered through the Whatman PTFE membrane and washed with de-ionized water till the pH reached close to 7 and then vacuum dried at room temperature.

The stock solution of PdCl₂ was prepared by first dissolving 0.0167 g of PdCl₂ in aqueous hydrochloric acid (26% v/v) under stirring at 353 K. After complete dissolution of PdCl₂, the solution was cooled to room temperature and then diluted to 100 mL by adding distilled water. 7.5 mL stock solution of Pd Cl₂ was then sonicated with 15 mg of CNT sample for 1 h. After 1 h, NaBH₄ (reducing agent) was added slowly until the solution became colourless and the catalyst was filtered and dried at 353 K for 3 h.

2.2.7. Supported Ni catalysts:

The monometallic nickel catalyst was prepared by an impregnation method. Slurry of 10 g of activated carbon was made in distilled water. To this hot slurry, a solution of Ni(NO₃)₂.6H₂O (4.95 g dissolved in 10 mL of water) was added. After stirring for 6 h, water was removed under vacuum using a rotary evaporator to obtain a solid cake. This solid was dried overnight at 383 K and calcined in a static air furnace at 723 K for 10 h. The reduction of the catalyst was carried out in an electric furnace using silica quartz tube at 723 K and at H₂ flow rate of 5 x 10⁻⁵ m³/min for 5 h. The catalyst was cooled under nitrogen flow of 3 x 10⁻⁵ m³/min. In a similar way, Ni catalyst supported on alumina was prepared.

2.2.8. Ni-Pt bimetallic catalyst:

A bimetallic Ni-Pt/C catalyst was prepared by addition of chloroplanic acid (H₂PtCl₄.6H₂O) to the already prepared Ni/C catalyst (see section 2.2.7). This suspension was refluxed for 4 h and then formaldehyde was added as a reducing agent. This solution was stirred further for 2 h and then filtered to give bimetallic Ni-Pt/C catalyst.
2.3. Physicochemical characterization of catalysts:
The prepared catalyst samples were characterized by various physico-chemical methods such as BET surface area analyzer, X-ray diffraction analysis, Raman spectroscopy, infrared spectroscopy, SEM, TEM, XPS and H₂ pulse titration. This section of chapter 2 gives a brief account of the theory and principles of various characterization techniques used for the current study. The procedure for each experimental technique is described. Characterization results are discussed in the relevant chapters.

2.3.1. Surface area measurement:
The Brunauer-Emmett-Teller (BET) is the most widely acceptable method for analyzing multilayer physisorption isotherms of inert gases to determine the surface area of solids and the distribution of mesopore size in these solids [1].
Surface area is calculated by comparing the integrator count due to desorption with that form the calibration signal the mass, W, adsorbed is given by equation (2.1)

\[ W = \frac{A}{A_{cal}} V_{cal} \frac{P_a M}{RT} \]  

\[ \text{…..2.1} \]

Where,
- \( W \) = mass of adsorbate adsorbed on the sample
- \( V_{cal} \) = calibration volume (cm³)
- \( A \) = sample integrator counts
- \( A_{cal} \) = calibration integrator counts
- \( P_a \) = ambient pressure
- \( M \) = adsorbate molecular weight (28 for N₂)
- \( T \) = temperature in K
- \( R \) = gas constant (82.06 cm³.atm.K⁻¹.mol⁻¹)

The BET equation (2.2) yields a straight line when \( 1/W(P/P_0) \) is plotted versus \( P/P_0 \). The slope, \( (C - 1)/W_mC \), and the intercept, \( 1/W_mC \), are used to determine the weight adsorbed at the monolayer.
\[
\frac{1}{W(P_0/P-1)} = \frac{C-1}{W_m C} \frac{P}{P_0} + \frac{1}{W_m C} 
\]

Where,
- \( W \) weight of adsorbate adsorbed at relative pressure \( P/P_0 \)
- \( P \) Partial pressure of adsorbate
- \( P_0 \) saturated vapor pressure of adsorbate
- \( W_m \) weight of adsorbate adsorbed at a coverage of one monolayer
- \( C \) a constant which is a function of the adsorbate heats of condensation and adsorption

The value of the slope \( S \) and the y-intercept \( i \) of the line are used to calculate the monolayer adsorbed gas quantity \( W_m \) and the BET constant \( C \), using the following equation.

\[
W_m = \frac{1}{S+i} 
\]

The total surface area of the sample, \( S_t \), is determined from equation (2.4),

\[
S_t = \frac{W_m NA_{cs}}{M_a} 
\]

Where,
- \( M_a \) adsorbate molecular weight
- \( W_m \) weight of adsorbate adsorbed at a coverage of one monolayer
- \( N \) Avogadro’s number = 6.023 \times 10^{23}
- \( A_{cs} \) cross sectional area of adsorbate molecule for \( N_2 \) gas 16.2 \times 10^{-20} \text{ m}^2

Specific surface \((\text{m}^2/\text{g})\) is given by equation (2.5),

\[
S_{BET} = \frac{S_t}{\text{weight of sample}} 
\]
BET surface areas of the specimen have been measured by using of N\textsubscript{2} adsorption at 77 K preformed on a Quantachrome CHEMBET 3000 instrument.

2.3.2. Temperature programmed reduction (TPR) method:
Temperature programmed reduction method is a technique in which a chemical reaction is monitored between metal particles and hydrogen gas while the temperature increases linearly with time. This method is used to find the most efficient reduction conditions for the catalyst. Catalyst precursor is subjected to a programmed temperature technique method while a reducing gas mixture (H\textsubscript{2}:N\textsubscript{2}) is flown over it.

In typical procedure, a U-tube (Quartz) was filled with the solid catalyst. This sample holder is positioned in a furnace which is equipped with a temperature controller. A thermocouple is placed in the U-tube for temperature measurements. Equal quantities of fresh vacuum dried catalyst were taken in the U-tube. Initially, U-tube was purged with inert gas (nitrogen) to remove the air present in the lines, and then heated to 250°C for 30 min in N\textsubscript{2} atmosphere with a flow rate of 60 ml/min in order to remove the moisture and surface impurities present on the sample, and then it was cooled to room temperature. The nitrogen was replaced by (5% H\textsubscript{2} in N\textsubscript{2}) for the TPR experiments. Mass flow controller was used to maintain the mixture of 5% hydrogen in nitrogen gas. Finally, the sample in the U-tube heated from 30°C to 500°C using a temperature controller, with the ramp rate of 15°C/min. The hydrogen consumed for complete reduction of the sample at certain temperatures, was detected by TCD, and was recorded.

2.3.3. H\textsubscript{2} pulse titration (chemisorption):
In our work, chemisorption of catalyst samples was carried out using Quantachrome make Chembet-3000 instrument, equipped with a thermal conductivity detector.

General experimental procedure for the pulse titration is given below

1. Accurately weighed (~0.050 g) sample was placed in a sample cell holder (Figure 2.2) and then the sample was heated under the flow of nitrogen gas at 200°C for 1 hour, by this treatment, the sample surface was cleaned and the moisture was completely removed.
2. After the sample was cooled to room temperature, the sample cell holder was connected to the spectrometer connection for pulse titration (see Figure 2.2).

3. Then the temperature was increased to 300°C by using temperature controller with a heating rate of 10°C/min in an inert atmosphere.

4. After attaining the temperature, nitrogen gas was replaced by a mixture of 5% hydrogen in nitrogen and kept it for half an hour.

5. Mixture of 5% hydrogen in nitrogen was replaced by nitrogen gas, kept it for 1 hour, and then cooled to room temperature. By this treatment, metal surface was cleaned and ready for the \( \text{H}_2 \) chemisorption analysis.

6. Using the calibrating syringe, 100 \( \mu \text{L} \) of the hydrogen gas was injected to the sample. This was repeated until three consecutive peaks with the same integrated area were obtained.

7. The volume of adsorbed hydrogen and metal dispersion at STP was calculated using TPR win software provided by Quantachrome.

\[\text{Figure 2.2. Quantachrome Chembet-3000 instrument}\]
2.3.4. X-ray diffraction:

Powder X-ray diffraction method is widely used for material characterization especially qualitative identification of crystalline phases. It provides the information about the identification of crystalline phases, lattice parameters, crystallite size measurement. It can detect crystalline materials having crystallites of greater than 3-5 nm and up to 100 nm.

The X-ray diffraction patterns are obtained by measurement of the angles by which an X-ray beam is diffracted by the sample. Bragg's equation relates the distance between two hkl planes (d) and the angle of diffraction (2θ) as given in equation 2.6 [2].

\[ n\lambda = 2dsin\theta \]  

Where,
- \( \lambda \) wavelength of the X-ray, nm
- \( n \) integer called order of the reflection
- \( d \) distance between two lattice plane
- \( \theta \) angle of incidence plane, degree

The average crystalline size of the metal particle can be estimated by Debey-Scherrer equation 2.7 [3].

\[ <L> = \frac{K\lambda}{\beta\cos\theta} \]  

In which,
- \( <L> \) is a measure for the dimension of the particle in the direction perpendicular to the reflecting plane
- \( \lambda \) is the X-ray wavelength, nm
- \( \beta \) is the peak width
- \( \theta \) is the angle between the beam and the normal on the reflecting plane, degree
- \( K \) is a constant i.e. (0.9)
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For calculation for peak width

\[ \beta = \sqrt{B_1^2 - B_2^2} \]  

Where,

- \( B_1 \) is the FWHM (full width half maxima)
- \( B_2 \) is the instrument broadening (0.15)

X-ray powder diffraction patterns have been recorded on a PANalytical PXRD Model X-Pert PRO-1712, using Ni filtered Cu Kα radiation (\( \lambda = 0.154 \) nm) as a source (current intensity, 30 mA; voltage, 40 kV) and a X-celerator detector. The samples were scanned in the 2\( \theta \) range of 5-80°. The species present on the surface were identified by their characteristic 2\( \theta \) values of the relevant crystalline phase.

2.3.5. X-ray photoelectron spectroscopy:

The X-ray photo electron spectroscopy [4-7] is based on the photoelectric effect, which involves the bombardment of a sample surface with X-ray and measurement of the concomitant photoemitted electrons. The photoemitted electrons have discrete kinetic energies that are characteristic of the emitting atoms and their bonding states. The shifts in core-level energies give information on the surface elemental composition, the oxidation state of the elements and chemical analysis [8].

The kinetic energy, \( E_k \), of these photoelectrons is determined by the energy of the X-ray radiation, \( h\nu \), and the electron binding energy \( E_b \) as given by,

\[ E_k = h\nu - E_b \]  

The experimentally measured energies of the photoelectrons are given by

\[ E_k = h\nu - E_b - \psi \]
Where,
\[ E_k \] is the kinetic energy of the photoelectron
\[ h \] is Plank’s constant
\[ \nu \] is the frequency of the exciting radiation
\[ E_b \] is the binding energy of the photoelectron with respect to the Fermi level of the sample
\[ \psi \] is the work function of the spectrometer

The shape of each peak and the binding energy can be slightly altered by the chemical state of the emitting atom. Hence, XPS can provide information on chemical bonding. The number of catalytic properties such as oxidation state of active species, interaction of a metal with a support, change in oxidation state upon activation of the catalyst, nature of surface impurities, can be studied by using this characterization technique. XPS measures the intensity of photoelectrons as a function of their kinetic energy.

X-ray photoelectron spectra were acquired on a VG Microtech Multilab ESCA 3000 spectrometer using a non-monochromatized MgKα X-ray source (\( h\nu = 1253.6 \text{ eV} \)). Base pressure in the analysis chamber was \( 4 \times 10^{-10} \text{ Torr} \). The errors in all the B.E. values were within \( \pm 0.1 \text{ eV} \). The binding energy correction was performed using the C\(_{1s}\) peak of carbon at 284.6 eV as the reference.

### 2.3.6. Fourier-transform infrared spectroscopy (FTIR):
In FTIR spectroscopy, the incident electromagnetic wave is absorbed by a molecule upon excitation of molecular vibration modes. Application of FTIR spectroscopy in catalysis is to identity adsorbed species and the way in which these species are chemisorbed on the surface of the catalyst [9]. The frequency of these vibrations depends upon the nature and binding of the molecules.

FTIR spectroscopy in the frame work region (400-4000 cm\(^{-1}\)) provides additional information to identify the adsorbed species and adsorbed reaction intermediates and their structures on catalyst surfaces [10].
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FTIR spectra was recorded on a Perkin-Elmer instrument. The pellets for analysis were prepared by mixing 3 mg of the catalyst with 50 mg of KBr. FTIR spectra were recorded between 450 to 4000 cm\(^{-1}\) with accumulation of 20 scan and 4 cm\(^{-1}\) resolution.

2.3.7. Transmission electron microscopy:
Transmission electron microscopy technique involves a primary electron beam of high energy and high intensity passing through a condenser to produce parallel rays, which impinge on the sample. As the attenuation of the beam depends on the density and the thickness, the transmitted electrons form a two-dimensional projection of the sample mass, which is subsequently magnified by the electron optics to produce a so-called bright field image. The dark field image is obtained from the diffracted electron beams, which are slightly off angle from the transmitted beam [11-14]. This technique allows the size distribution, external morphology, chemical composition and shape of metal particles in supported and unsupported catalyst to be characterized down to the level of atomic resolution better than 0.5 nm [10].

Operating conditions of a TEM instrument is 100-200 keV electrons, \(10^{-6}\) mbar vacuum, 0.5 nm resolution and a magnification of \(3 \times 10^5\) to \(10^6\). TEM analysis was performed on a Jeol Moeld JEM 1200 electron microscope operated at an accelerating voltage of 120 kV. A small amount of the solid sample was sonicated in methanol for 1 min. A drop of prepared suspension was deposited on a Cu grid coated with carbon layer and grid was dried at room temperature before analysis.

2.3.8. Scanning electron microscopy:
Scanning electron microscopy is a technique to probe the morphological features of catalyst materials. SEM scans over a sample surface with a probe of electrons (5-50 eV) and detects the yield of either secondary or backscattered electrons as a function of the position of the primary beam. Contrast is generally caused by the orientation such that the part of the surface facing the detector appears brighter than the part of the surface with its surface normal pointing away from the detector. The interaction between the electron beam and the sample produces different types of signals providing detailed information about the surface structure and morphology of the sample [15]. When an electron from
the beam encounters a nucleus in the sample, the resultant Coulombic attraction leads to a deflection in the electron's path, known as Rutherford elastic scattering. A fraction of these electrons will be completely backscattered, re-emerging from the incident surface of the sample. Since the scattering angle depends on the atomic number of the nucleus, the primary electrons arriving at a given detector position can be used to produce images containing topological and compositional information [16]. A major advantage of SEM is that bulk samples can also be directly studied by this technique.

The chemical composition of the sample was determined by energy dispersion X-ray (EDX) attached to a scanning electron microscopy (SEM: JEOL JSM 500).

2.3.9. Raman spectroscopy:
Raman spectroscopy is based on the inelastic scattering of photons, which loses energy by exciting vibrations in the sample [17]. Raman spectroscopy is generally used for characterizing the materials to find the crystallographic orientation of a sample, chemical structure of molecules. It allows studying surface metal oxide species on typical oxide support materials. It offers to study the molecular vibrations below 1100 cm\(^{-1}\) [17]. The radial breathing mode is commonly used technique to evaluate the diameter of sample and used to understand the structure of the composition.

The Raman spectra of sample were recorded on a Horiba JY LabRAM HR800 micro-Raman spectrometer with 17 mW 632.8 nm laser excitation.

2.4. Catalyst activity measurement:
2.4.1. Continuous high pressure reactor setup:
Bench scale continuous hydrogenation experiments were carried out in a high-pressure, fixed-bed reactor supplied by M/s. Geomechanique, France. A schematic of the reactor setup is shown in Figure 2.3. It consisted of stainless steel tube of 0.35 m length and 1.5 x 10\(^{-2}\) m inner diameter that was heated by two tubular furnaces whose zones (TIC1 and TIC2) were independently controlled at the desired bed temperature. The reactor was provided with two thermocouples [Chromel-Alume thermocouples (type K)] to measure the temperature at two different points. The reactor was equipped with mass flow controllers, pressure indicator, and controller (PIC) devices. A storage tank was
connected to the metering pump through a volumetric burette to measure the liquid flow rate. The pump had a maximum capacity of $3 \times 10^{-4}$ m$^3$/h under a pressure of 10 MPa. The gas outlet line was equipped with a backpressure controller, which maintained a constant pressure in the unit by continuous pressure release. The other end of the reactor was connected to a gas-liquid separator through a condenser. The experiments were carried out over 10 and 20 g of catalyst in the form of pellets having 4 mm diameter. The section 5 cm and 5 cm below the catalyst bed was packed with inert packing (carborundum), thus providing the catalyst bed depth of ~25 m. The reactor was flushed thoroughly with H$_2$ at room temperature before the start of the actual experiment. After attaining the desired temperature, the reactor was pressurized with H$_2$. The liquid feed was “switched on” after the reactor has reached the operating pressure and kept there for 1 h to obtain the constant liquid flow rate. Liquid samples were withdrawn at regular intervals of time and were analyzed by gas chromatography.
2.4.2. Batch reactor set up:

All the batch hydrogenation experiments were carried out in a 300 mL capacity stirred autoclave supplied by Parr Instruments Co. USA, which was equipped with heating arrangement, overhead stirrer, thermo well, internal cooling coil, gas inlet and outlet, liquid sampling valve, safety rupture disc, pressure gauge as well as transducer for digital pressure display, separate automatic controller to control the temperature, agitation speed, solenoid valve and high temperature cutoff module. Water circulation through the internal cooling loop equipped with automatic cut-off arrangement controlled the temperature inside the reactor with an accuracy of ±1°C. A schematic of the batch slurry reactor set-up is shown in Figure 2.4.

In a typical hydrogenation experiment, required amount of substrate was charged into the reactor. Total volume of the liquid phase was always kept to 100 mL by adding...
appropriate solvent and the required amount of slurry of catalyst was charged in an autoclave carefully and reactor vessel was closed. The contents were first flushed 2-3 times with N\textsubscript{2} gas for the removal of trapped air and then flushed with H\textsubscript{2}. Then the temperature was ramped to the required temperature. After attaining the desired temperature, the system was pressurized with H\textsubscript{2} gas to the desired pressure. Initial liquid sample was withdrawn before starting the reaction, by switching the stirrer on and the progress of the reaction was monitored by observing the pressure drop in the reservoir as a function of time. When the reaction was over, as indicated by a constant H\textsubscript{2} pressure on the pressure display, the reactor was cooled to room temperature and excess H\textsubscript{2} gas was vented out safely and the reactor contents were discharged. Samples were withdrawn at regular time intervals for the analysis using gas and liquid chromatography.
Figure 2.4. Parr reactor setup

(1) Reactor (2) stirrer shaft (3) impeller (4) cooling water (5) sampling valve (6) magnetic stirrer (7) electric furnace

T1: Thermocouple P1: Pressure transducer T1g: Thermocouple for gas N: Nitrogen cylinder H2: Hydrogen gas cylinder PR: Pressure regulator CPR: Content pressure regulator TR1: Reactor temperature indicator PR1: Reactor pressure indicator TR2: Reservoir temperature Indicator TRg: Gas temperature indicator PR2: Reservoir pressure indicator

2.4.3. Atmospheric reaction set up:

Hydrogenation of phenylacetylene was conducted at atmospheric pressure, in a 250 mL capacity three-necked glass reactor fitted with a cooling condenser (Figure 2.5). In a typical experiment, phenylacetylene (49 mmol), and methanol (90 mL) were charged to the reactor and the system was purged with N2 for 10 min. To this, 5 ml of colloidal Pd
catalyst was added and the hydrogenation was started by bubbling H₂ gas at a desired flow rate through the reaction mixture and the H₂ flow was regulated by a needle valve (30 mL/min). This time was considered as the start of the catalytic reaction. All the reactions were performed up to 100% conversion, and this was taken as the end of the reaction. Agitation was carried out with a magnetic stirring bar. Timely samples were taken and analyzed on GC.

Figure 2.5. Atmospheric reactor setup
2.5. Analytical methods:

Chromatography:
Chromatography is a separation process that is achieved by distributing the components of a mixture between two mutually immiscible phases, one phase is stationary and other is mobile. A sample component introduced in a mobile phase carried along with a column containing a distributed stationary phase. The species of sample undergo repeated interactions between the mobile phase and stationary phase. Those components held preferentially in the stationary phase are retained longer in the system than those that are distributed selectively in the mobile phase. Separation can be achieved by selection of both phases, and the sample component gradually separated in bands in the mobile phase. As a consequence, solutes are eluted from the system as local concentrations in the mobile phase in the order of their increasing distribution coefficients with respect to the stationary phase: the least retained component emerges first; the most strongly retained component elutes last [18, 20].

Applications:
Depending on mobile phase the chromatographic techniques are divided into two parts
- Gas chromatography
- Liquid chromatography

1. Gas Chromatography:
In gas chromatography, inert gas used as a mobile phase e.g. He, H₂, N₂ and analysis sample must be thermally stable and volatile that of organic/inorganic compounds. Column is heart of chromatography where actual separation is take place. The details of stationary phases used for the quantitative and qualitative analysis are shown in Table.
Table 2.1. Selected stationary phases used for gas-liquid chromatography analysis.

<table>
<thead>
<tr>
<th>Column trade name &amp; Column details</th>
<th>Stationary phase</th>
<th>Operating range /limit</th>
<th>Compounds analyzed in this work</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HP-FFAP,</strong> <em>(Free Fatty acid phase column)</em> 30 m x 0.53 mm x 1.0 µm*</td>
<td>5% methylpolysiloxane + polyethylene glycol <em>(Nitroterephthalic acid modified polyethylene glycol)</em></td>
<td>60 - 250°C</td>
<td>Used for the analysis of 2-butyne-1,4-diol, 2-butene-1,4-diol, butanediol</td>
</tr>
<tr>
<td><strong>HP-1</strong> 30 m x 0.32 mm x 1 µm*</td>
<td>100% Dimethylpolysiloxane, Non polar</td>
<td>325/350°C</td>
<td>Nitrobenzene, aniline, m-, p-, o-chloronitrobenzene, m-, p-, o-chloroaniline,</td>
</tr>
<tr>
<td><strong>HP-5</strong> 30 m x 0.32 mm x 1 µm*</td>
<td><em>(5%-Phenyl)-methylpolysiloxane, Non-polar</em></td>
<td>-60 - 325°C</td>
<td>Phenylacetylene, styrene, ethylbenzene</td>
</tr>
</tbody>
</table>

* Column length x column ID x film thickness

Hewlett-Packard model equipped with flame ionization detector (FID) was employed for the analysis of samples. Major advantages of FID include a detection limit that is approximately two to three orders of magnitude smaller than that for a thermal conductivity and helium gas used as a carrier. On basis of plot of response Vs time, the qualitative and quantitative analysis were determined by using gas chromatography.

2. High performance liquid chromatography:

Hewlett-Packard model 1050 liquid chromatograph equipped with an ultraviolet detector and HP 1100 series auto sampler was employed for the analysis of liquid samples. HPLC
analysis was performed on a 25 cm RP-18e\* column supplied by Hewlett-Packard. The products and reactants were detected using a UV detector at $\lambda_{\text{max}}$, 254 nm using 30\% acetonitrile:5\% Buffer:water as the mobile phase at a column temperature of 313 K and flow rate of 1 mL/min. Samples of 10 µL were injected into the column using an autosampler.

<table>
<thead>
<tr>
<th>HPLC analysis Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Column Details</strong></td>
</tr>
<tr>
<td>Dimensions (Length, ID)</td>
</tr>
<tr>
<td>Particle size</td>
</tr>
<tr>
<td>Stationary Phase</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Mobile Phase analysis details</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobile Phase</td>
</tr>
<tr>
<td>Flow rate</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Sample volume</td>
</tr>
<tr>
<td>Washing Phase</td>
</tr>
<tr>
<td>HPLC column washing mobile phase Flow rate</td>
</tr>
<tr>
<td>Detector</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
</tr>
</tbody>
</table>
Calculation for response factor, % conversion and % selectivity:

\[
R_f = \frac{\text{Concentration in moles}}{\text{area under the respective peak}}
\]  

\[
\% \text{ Conversion} = \frac{\text{Initial moles of substrate} - \text{Final moles of substrate}}{\text{Initial moles of substrate}} \times 100
\]  

\[
\% \text{ Selectivity} = \frac{\text{moles of product formed}}{\text{moles of substrate consumed}} \times 100
\]
2.6. References:
