CHAPTER-II

EXPERIMENTAL
2.1 CATALYST PREPARATION

Two series of ferrospinels of formulae $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ and $\text{Co}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7$ and $1$) and their sulphated analogues were prepared for the present work. Their compositions and cation distributions are summarised in the following table.

Table 2.1 Catalyst compositions and cation distributions of ferrospinels containing Co, Ni and Cu.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Composition</th>
<th>Cation at Tetrahedral site</th>
<th>Cation at Octahedral site</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$\text{NiFe}_2\text{O}_4$</td>
<td>$\text{Fe}^{3+}$</td>
<td>$\text{Fe}^{3+}\text{Ni}^{2+}$</td>
</tr>
<tr>
<td>0</td>
<td>$\text{CoFe}_2\text{O}_4$</td>
<td>$\text{Fe}^{3+}$</td>
<td>$\text{Fe}^{3+}\text{Co}^{2+}$</td>
</tr>
<tr>
<td>1</td>
<td>$\text{CuFe}_2\text{O}_4$</td>
<td>$\text{Fe}^{3+}$</td>
<td>$\text{Fe}^{3+}\text{Cu}^{2+}$</td>
</tr>
</tbody>
</table>

Mixed Ferrospinels

- i) Ni–Cu series
  - 0.3 $\text{Ni}_{0.7}\text{Cu}_{0.3}\text{Fe}_2\text{O}_4$ | $\text{Fe}^{3+}$ | $\text{Fe}^{3+}\text{Ni}_{0.7}^{2+}\text{Cu}_{0.3}^{2+}$ |
  - 0.5 $\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ | $\text{Fe}^{3+}$ | $\text{Fe}^{3+}\text{Ni}_{0.5}^{2+}\text{Cu}_{0.5}^{2+}$ |
  - 0.7 $\text{Ni}_{0.3}\text{Cu}_{0.7}\text{Fe}_2\text{O}_4$ | $\text{Fe}^{3+}$ | $\text{Fe}^{3+}\text{Ni}_{0.3}^{2+}\text{Cu}_{0.7}^{2+}$ |

- ii) Co–Cu series
  - 0.3 $\text{Co}_{0.7}\text{Cu}_{0.3}\text{Fe}_2\text{O}_4$ | $\text{Fe}^{3+}$ | $\text{Fe}^{3+}\text{Co}_{0.7}^{2+}\text{Cu}_{0.3}^{2+}$ |
  - 0.5 $\text{Co}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$ | $\text{Fe}^{3+}$ | $\text{Fe}^{3+}\text{Co}_{0.5}^{2+}\text{Cu}_{0.5}^{2+}$ |
  - 0.7 $\text{Co}_{0.3}\text{Cu}_{0.7}\text{Fe}_2\text{O}_4$ | $\text{Fe}^{3+}$ | $\text{Fe}^{3+}\text{Co}_{0.3}^{2+}\text{Cu}_{0.7}^{2+}$ |

Preparation of these systems was done by the 'soft' chemical route reported by Date et al. [1]. Extra pure grade $\text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$, $\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$, $\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O}$ and $\text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$ from Merck were used as such, without further purification. Metals were coprecipitated as their hydroxides from their nitrate solutions using sodium hydroxide as the precipitating alkali. Stoichiometric masses of the nitrates
were accurately weighed out and dissolved in distilled water to the following molarities.

1. ferric nitrate: 2.6 M
2. cobalt nitrate: 3.4 M
3. Nickel nitrate: 3.4 M
4. Copper nitrate: 3.4 M

Solutions of the metal nitrates were mixed thoroughly and the mixture was added rapidly to stoichiometric amount of 5.3M NaOH solution with stirring. Temperature of the slurry rose to 45-50°C due to the exothermic nature of the precipitation reaction. The pH of the final slurry was carefully adjusted between 10 and 11. The precipitate was kept overnight for aging and then washed several times (about 10-12 washings) with distilled water until free from nitrate ion and alkali. It was filtered and then dried in an air oven at 120°C for 48 hours and was calcined at 300°C for 3 hours to achieve transformation into spinel phase. The dried materials were powdered and sieved below 75 µm mesh.

Sulphation of spinel samples was done by the standard ‘impregnation’ method. 30 g of each of the spinel oxide samples was immersed in 150 ml of 0.2 M \((\text{NH}_4)_2\text{SO}_4\) solution and mechanically agitated for 4 hours. The mixture was kept overnight and filtered without washing. It was then dried at 120°C for 24 hours, powdered and sieved below 75 µm mesh.

2.2 CATALYST CHARACTERISATION

The prepared catalyst samples were characterized by adopting a variety of physico-chemical methods. Before each characterization, the samples were activated for 3 hours at temperatures of 300°C or 500°C. A brief discussion of each method of characterisation along with the experimental aspects adopted is presented below.

2.2.1 X-ray Diffraction analysis

X-ray diffraction (XRD) by crystals is the most widely employed method for determining the three dimensional structure of solid substances. Complete determination of crystal structure by locating the coordinates of all the atoms needs good single crystals at least of the size of about 1 mm. Most commonly found solids
are however, polycrystalline, meaning that each particle is made up of a large number of randomly oriented tiny crystals [2]. It is possible to get important structural information by recording the X-ray diffraction pattern of powdered polycrystalline samples by the powder diffractometer method.

Monochromatic X-rays (like Cu Kα or Mo Kα source) are reflected by families of planes in the polycrystalline material when the Bragg equation, \( 2d \sin \theta = n\lambda \), is fulfilled, where \( d \) is the interplanar spacing, \( \theta \) is the angle between the planes and the X-ray beam (Bragg angle), \( \lambda \) is the X-ray wave length, and \( n \) is an integer called the order of reflection. Families of planes are identified by a system of Miller indices, \( hkl \). These are integers and correspond to the number of times a family of planes strike the \( a, b, \) and \( c \) edges of the unit cell.

Powder diffractometer can produce accurate data in less than half an hour. The specimen for diffraction studies is prepared by packing the powder into the window of an aluminium holder backed by a glass slide. The plate containing the specimen is rotated and the diffracted X-rays are detected using a proportional counter or scintillation counter, rotating at twice the speed of the specimen. The usual scan speed is \( 2\theta \) per minute. The X-rays reaching the detector are registered and displayed on a paper chart recorder as series of peaks on top of background due to 'white' radiation, together with a scale of \( 2\theta \). The Bragg angles are simply read off the diffractometer trace and rough values of relative intensity are derived from peak heights above background.

Every crystalline substance has a unique X-ray powder pattern because line positions depend on unit cell size, and line intensity depends on the type of atoms present and on their arrangement in the crystal. Materials are identified from these values in conjunction with the 'Joint Committee on Powder Diffraction Standards' (JCPDS) Powder Diffraction File. This contains sets of cards containing X-ray data for most known crystalline phases. The data include \( d \)-spacing and relative intensity (\( I/I_0 \)) values, Miller indices, unit cell dimensions etc. The appropriate Data Card is retrieved and the experimental data, especially those of the three strongest peaks are matched with the standard values [3].
Powder diffractometer method has many other applications than qualitative phase analysis. Some of these are quantitative phase analysis, determination of unit cell parameters, study of preferred orientation and the determination of particle size [3].

Rough estimate of particle size less than 0.1 μm diameter can be obtained from the amount of line broadening using the relation,

\[ t = \frac{\lambda}{B \cos \theta} \]

where \( B \) = line width (Full Width-Half Maximum) of the strongest peak (in radians), \( \theta \) = Bragg angle and \( t \) = the crystal diameter. The line broadening gives the size of the crystals and not the size of the particles since a particle may contain a number of crystals [4].

The diffractometer traces of the catalyst samples were taken using RIGAKU D/MAX-C instrument.

2.2.2 Infrared Spectroscopy

Infrared (IR) spectroscopy has been widely used in catalysis for identifying the structural features of the catalyst itself, as well as for identifying the adsorbed species and reaction intermediates on the catalyst surface. Conventional dispersive infrared spectrometers are gradually being replaced by Fourier Transform Infrared (FTIR) instruments due to many added advantages like improved spectral quality, higher sensitivity, suitability for use in the low frequency region (<600 cm\(^{-1}\)) etc. In FTIR, a polychromatic incoming infrared beam passes through an interferometer, the sample and reaches the detector to produce an interferogram where the spectral information is in the line domain. It is converted to frequency domain spectral data using Fast Fourier Transform done with a computer attached to the instrument. The sampling of solids for infrared studies are most commonly done as KBr pellets or wafers.

The introduction of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) by Fuller and Griffiths [5] in 1978 has revolutionised the
application of IR spectroscopy to yield valuable spectroscopic information inherent in a mid-IR (4000-200 cm\(^{-1}\)) spectrum. Diffuse reflectance differs from ordinary reflectance, in that, here, the angular distribution of the reflected radiations is independent of the angle of incidence. A diffuse reflectance spectrum is obtained by the collection and analysis of surface-reflected electromagnetic radiation as a function of frequency using Fourier Transform technique. Thus it is more sensitive to surface species than the bulk of particles and hence is most suitable to explore the surface chemistry of high surface area powders. DRIFTS enables the rapid identification of powders with little or no sample preparation and a very little (about 0.1 mg) amount of the sample. Thus, for a variety of reasons, DRIFTS is becoming the single most important technique of studying the surfaces of catalyst powders [6].

The IR spectra of the catalyst samples have been taken in order to identify sulphation and to reaffirm the identification of the spinel phase. Ferrospinels typically give two absorption bands below 1000 cm\(^{-1}\) [7] and sulphated samples typically show a number of weak bands in the range 900-1100 cm\(^{-1}\) and sometimes, a strong band near 1380 cm\(^{-1}\) [8].

The FTIR spectra were taken using Shimadzu FTIR-8101 and the DRIFT spectra were taken using a DR-IR (Shimadzu).

2.2.3 BET Surface area determination

The Brunauer, Emmett and Teller (BET) method [9] has been adopted as a standard procedure for surface area determination of powdered catalysts. The BET theory of adsorption is an extension of Langmuir model to multilayer adsorption. The basic assumptions of the BET model are (i) the heat of adsorption for an adsorbate-adsorbent system does not change with surface coverage which means that all the adsorption sites on a given surface are energetically homogeneous (ii) the adsorption is multilayer and the heat of adsorption of the second and the subsequent layers are the same as the heat of condensation of the adsorbate and (iii) the model assumes a dynamic equilibrium within each layer.
The BET equation is conveniently expressed in the form,

\[ \frac{p}{[v \,(p_0 - p)]} = \frac{1}{Cv_m} + \left[ \frac{(C - 1)}{(v_mC)} \right] \left( \frac{p}{p_0} \right) \]

where \( C \) = a constant for a given system at a given temperature and related to the heat of adsorption, \( v \) = the volume adsorbed at equilibrium pressure \( p \), \( v_m \) = volume of the adsorbate necessary to form a monolayer on the surface, and \( p_0 \) = saturated vapour pressure of the adsorbate.

This equation predicts a linear plot (BET plot) between the experimental \( \frac{p}{[v \,(p_0 - p)]} \) and \( \frac{p}{p_0} \) values with slope equal to \( \frac{(C - 1)}{(v_mC)} \) and y-intercept equal to \( \frac{1}{(Cv_m)} \). From the slope and intercept, \( v_m \) can be calculated. The specific surface area of the sample is then calculated using the relation,

\[ \text{Surface area (m}^2\text{ g}^{-1}) = \frac{v_m}{N_0 \cdot \frac{a_m}{(22414 \text{ wt})}} \]

where \( a_m \) = average area occupied by the adsorbate molecule,
\( N_0 \) = Avagadro number and
\( \text{wt} \) = mass of the solid sample used for surface area measurements.

Adsorption of nitrogen gas at its boiling point is generally used for surface area measurements using BET method, \( a_m \) for \( N_2 \) being taken as 0.162 nm\(^2\). The linearity of BET plot is severely restricted to within the \( p/p_0 \) range of 0.05 - 0.30. A very high or very low \( C \) value will create considerable error in calculating the effective adsorbate cross-sectional area. High \( C \) values are likely to be associated either with localised monolayer adsorption or with micropore filling. Best results are obtained if \( C \) values are within the approximate range 80-120 [10].

The surface areas of all the catalyst samples have been measured by BET nitrogen adsorption at liquid \( N_2 \) temperature using the Micromeritics Gemini Analyser.

2.2.4 Pore Volume determination using mercury porosimetry

Dubinin [11] has classified pores according to their diameters as micropores (<20Å), macropores (>200Å), and intermediate pores, now called mesopores (between 20 and 200 Å). The pore size can be determined either from an adsorption isotherm or by using a mercury porosimeter. The underlying principle of mercury
porosimeter is to relate the force necessary to intrude a non-wetting liquid like mercury, to the average radius of the pores which are filled. The number of these pores is related to the volume of mercury needed to fill pores of certain average diameter. The relationship among the pressure($\Delta P$), surface tension($\gamma$), contact angle($\theta$) and pore radius($r_p$) is given by [12],

$$\Delta P = -\frac{2\gamma \cos \theta}{r_p}$$

For mercury, $\gamma = 480$ dyne cm$^{-1}$ and $\theta = 140^\circ$ so that the above equation enables one to calculate the pressure that will be needed to force mercury into pores of radius $r_p$. The apparatus consists of a calibrated piston pump, connected to a thermostated high pressure cell and a pressure gauge. The zero penetration volume is noted when the pressure just begins to rise. Usually these instruments are automated such that the volume and pressure signals drive an X-Y recorder or the data are collected on computer for post-run processing and manipulation.

The pore volumes of the catalyst specimens were determined using a Quantachrome mercury porosimeter.

2.2.5 Energy Dispersive X-ray (EDX) fluorescence analysis and Scanning Electron Microscope (SEM)

Energy dispersive X-ray (EDX) fluorescence analysis is a relatively new analytical technique used for qualitative and quantitative elemental analysis of solid specimens. As the name implies, it separates the characteristic X-rays on the basis of their photon energies rather than on their wave lengths. The instrumentation has been made possible due to the simultaneous development of the Si(Li) detector, the multi-channel pulse height analyser and powerful microcomputers [13].

The Si(Li) detector cooled by liquid N$_2$ receives undispersed characteristic X-rays from a fluorescing specimen. The amplified detector output is then digitised and the pulses accumulated in channels, each channel representing a small range of energy. For quantitative analysis, data are transferred to a computer for the calculation of elemental concentrations. For qualitative analysis the data may be displayed in a number of ways, eg, as a series of peaks (intensity vs. energy) on a cathode ray oscilloscope.
The compact geometry of the spectrometer allows the use of low power X-ray tubes and results in specimen preparation not being very critical. The simultaneous measurement and display of the energy spectrum result in rapid quantitative and qualitative elemental analysis. However, the method has some limitations, mainly imposed by the Si(Li) detector. The technique cannot detect elements lighter than sodium and the resolution of low energy radiation is poor. Again, it is not possible to achieve high sensitivities of weak peaks when strong ones are also present.

Scanning Electron microscopy (SEM) is based on the strong interaction of electrons with matter and their appreciable scattering by quite small atomic clusters. Electrons can be conveniently deflected and focused by electric or magnetic fields so that magnified real-space images can be formed in addition to simple diffraction patterns. In SEM, the electron optics act before the specimen is reached to convert the beam into a fine probe which can be as small as 100 Å in diameter at the specimen surface [14]. This enables very impressive, in-focus images to be obtained from the highly irregular structures typical of catalyst specimens. The technique is of great interest in catalysis particularly because of its high spatial resolution. However, a serious drawback is that, the result need not be really representative of the whole sample. This can be overcome by making many analyses at different locations of the sample particles and for many catalyst particles.

SEM analysis was done using Stereoscan 440: Cambridge, U.K. Scanning Electron Microscope.

2.2.6 Mossbauer spectroscopy.

Mossbauer spectroscopy has matured into an important technique for catalyst characterisation, although its application is limited to a small number of Mossbauer-active elements among which iron, tin, europium, iridium, ruthenium, antimony, platinum and gold are probably the most relevant for catalysis [15]. This technique yields information's like oxidation state, magnetic properties and lattice symmetry of these elements in catalyst specimens. The use of specimens in the form of micro
crystallites ensures that the information obtained bears considerable significance to the chemical state of the surface of the catalyst [16]. The great advantage of Mossbauer spectroscopy is that its γ-ray photons 'see' inside reactors to reveal catalyst chemistry and structure under in situ conditions of high temperature and pressure.

Mossbauer spectroscopy is based on Mossbauer effect, the recoil-free γ-ray emission and resonant absorption as achieved by putting the emitting and absorbing nuclei within a rigid solid matrix. Its importance lies in the very narrow line width of the γ-ray spectrum. Consequently it is able to probe the minor variations in nuclear energy levels resulting from any discrete changes in the chemical state and/or environment of the Mossbauer nucleus.

The most widely studied Mossbauer isotope is $^{57}$Fe having a natural abundance of around 2%. The Mossbauer spectrometer essentially consists of a γ-ray source attached to a Doppler-shifting device, the sample (absorber) and a detector (G.M counter) which is connected to an amplifier and then to a pulse generator. The source of γ-rays is excited $^{57}$Fe nuclei, produced by the decay of $^{57}$Co isotope. These excited $^{57}$Fe nuclei, in turn, decay in various modes emitting γ-rays of which the 14.4 keV γ-ray is of interest in Mossbauer spectroscopy. For scanning the minor energy changes in the sample nuclei, the source γ-ray energy is modified by Doppler shift generated by the controlled movement of the source. Thus Mossbauer spectrum consists of a plot of counts vs the applied Doppler velocity in the range of -10 to +10 mm s⁻¹.

The three important Mossbauer parameters are (i) isomer shift, (ii) the electric quadrupole splitting, $\Delta E_Q$ and (iii) the magnetic hyperfine splitting.

The isomer shift, $\delta$, is the consequence of the Coulomb interaction between the positively charged nucleus and the negatively charged s-electrons which have definite density within the nuclear volume. Since the size of the nucleus in the excited state differs from that in the ground state, the Coulomb interaction energies are different as well. The isomer shift, therefore, is a measure of the s-electron
density at the nucleus, and yields useful information on the oxidation state of the iron in the absorber. Isomer shifts are expressed in velocity units, mm/s, and are given with respect to the peak position of a reference such as metallic iron or sodium nitroprusside.

The electric quadrupole splitting, $\Delta E_Q$, is caused by the interaction of the electric quadrupole moment of the nucleus with an electric field gradient (EFG). The nucleus of iron in the excited state has the shape of an ellipsoid and possesses an electric quadrupole moment. The origin of EFG is twofold. It is caused by asymmetrically distributed electrons in incompletely filled shells of the atom itself and by charges on neighbouring ions. If the symmetry of the electrons is spherical and that of the surrounding ions is cubic, EFG vanishes.

The magnetic hyperfine splitting, also known as the Zeeman effect, arises from the interaction between the nuclear magnetic dipole moment and the magnetic field $H$ at the nucleus. This interaction gives rise to six transitions (magnetic sextuplet) with the separation between the corresponding peaks in the spectrum proportional to the magnetic field at the nucleus.

Often, all these three interactions occur simultaneously. In catalysts, the usual situation is that the quadrupole interaction is much smaller than the magnetic interaction. Again, Mossbauer lines may be broad, overlapping and ill-resolved and various curve fitting methods are then used to sort out the situation.

Yet another application of Mossbauer spectroscopy is to determine particle size. If the particle size is very small, a ferro or ferrimagnetic specimen fails to show magnetic splitting at room temperature. This is because the thermal excitations of energy $kT$ at room temperature are energetic enough to decouple the magnetisation from the lattice causing the magnetisation vector of each particle to fluctuate rapidly over all directions. Thus the Mossbauer nucleus feels an average magnetisation of zero and a singlet or a doublet (in the case of quadrupolar splitting) Mossbauer spectrum, characteristic of superparamagnetic substance, results [17]. Now the particle size can be determined by studying the Mossbauer spectrum of the
superparamagnetic substance at varying temperatures and/or applied magnetic fields [17]. Shift from superparamagnetic singlet to ferro or ferrimagnetic sextet Mossbauer spectra is often found as the measuring temperature is lowered because the critical particle size to maintain magnetic property becomes smaller at lower temperatures [18].

The Mossbauer spectra of the catalyst samples have been taken using the constant acceleration type Austin (USA) S-600 Mossbauer spectrometer.

2.2.7 Thermogravimetric analysis (TGA)

Thermogravimetry is a technique where the weight of a sample can be followed over a period of time while its temperature is being raised linearly. Recording analytical balances with provision for controlled heating of a sample are called thermobalances. In a thermogravimetric curve the horizontal portions point out the regions where there is no weight change, whereas the weight loss is indicated by the curved portions. In the derivative thermogravimetric curve (DTG), dips correspond to weight loss and plateaus correspond to no weight change.

The TGA of catalyst samples has been done using TGA – 50 (Shimadzu) at the rate of heating of 10° per minute.

2.3 DETERMINATION OF SURFACE ELECTRON-DONOR PROPERTIES

(a) Reagents and purification methods:

The electron acceptors used in the study are:

7,7,8,8 -tetracyanoquinodimethane (TCNQ)
2,3,5,6 -tetrachloro-p-benzoquinone (chloranil) and
p-dinitrobenzene.

TCNQ was obtained from Merck -Schuchandt and was purified by repeated recrystallisation from acetonitrile [19]. Chloranil was obtained from Sisco research laboratories Pvt. Ltd. and was purified by recrystallisation from benzene [20]. p - Dinitrobenzene was supplied by Koch Light laboratories Ltd. and was purified by recrystallisation from chloroform [21].
Acetonitrile was used as the solvent. SQ grade acetonitrile obtained from Qualigens Fine Chemicals was first dried by passing through a column filled with silica gel 60-120 mesh size activated at 110°C for 2 hours. It was then distilled with anhydrous phosphorus pentoxide and the fraction distilling between 80-82°C was collected [22].

(b) Method adopted for adsorption studies:

The catalyst was activated at a particular temperature for 3 hours prior to each experiment. Adsorption study was carried out over 0.5 g catalyst placed in a cylindrical glass vessel fitted with a mercury sealed stirrer. Before sealing, the sample was outgassed at 10 torr for one hour. 10 mL of solution of an electron acceptor in acetonitrile was then admitted to the catalyst. Stirring was continued for 4 hours in a mechanically driven stirrer at 28°C in a thermostated bath and the oxide was collected by centrifuging the solution. The amount of electron acceptor adsorbed was determined from the difference in the concentration of the electron acceptor in solution before and after adsorption, which was measured by means of a Shimadzu UV - VIS spectrophotometer. The $\lambda_{max}$ of electron acceptors in acetonitrile are 393.5 nm for TCNQ, 288 nm for chloranil and 262 nm for p-dinitrobenzene. From the absorbance vs. concentration linear plots, any unknown concentrations have been determined.

2.4 ACIDITY DETERMINATION BY GRAVIMETRIC ADSORPTION OF n-BUTYLAMINE

Determination of the strength of the acidic sites exposed on the solid surface as well as their distribution is a necessary requirement to understand the catalytic properties of solid acids. Among all the physico-chemical methods of determining acidity as reviewed by Kijenski and Baiker [23], temperature-programmed desorption and calorimetric measurements are the most promising. However, the gravimetric adsorption of n-butylamine followed by TGA is a very simple method to determine strength and distribution of acid sites on catalyst surfaces [24,25].

Catalysts were kept in a desiccator saturated with n-butylamine vapour at room temperature for 48 hours. Then the weight loss of the adsorbed sample was
measured by TGA (Shimadzu TGA-50) operating between 40 to 600°C at a rate of 20°/minute. The weight loss between 150-300, 301-450 and 451-600°C are considered to be measures of weak, medium and strong acid sites, respectively.

2.5 VAPOUR-PHASE CYCLOHEXANOL DECOMPOSITION REACTION

Cyclohexanol from Merck was used as such without further purification. The reaction was done at atmospheric pressure in a fixed bed, vertical, down-flow, integral silica reactor placed inside a double-zone furnace (Solelem - France). Schematic diagram of the reactor set up is shown in Fig 2.4.1. The catalysts were pressed, pelletised and broken into uniform pieces and sieved to obtain catalyst particles of size 10-20 mesh. Exactly 3 g catalyst was charged each time in the centre of the reactor in such a way that the catalyst was sandwiched between the layers of inert porcelain beads. The upper portion of the reactor served as a vapouriser cum pre-heater. All heating and temperature measurements were carried out using 'Aplab' temperature controller and indicator instruments.

A thermocouple was positioned at the centre of the catalyst bed to monitor the exact temperature of the catalyst bed. The catalysts were activated in the reactor itself at 573K in a sufficient flow of dry air or at least 3 hours before each run. The liquid reactant was fed by a syringe pump (ISCO Model 500 D). The products of the reaction were collected downstream from the reactor in a receiver connected through a cold water circulating condenser. Products were collected at various time intervals and analysed by gas chromatography (Shimadzu, Model 15A, HP ultra capillary column, FID detector, N2 carrier gas, injection port temperature 250°C, column temperature 80°C, detector temperature 250°C.) Identification of products was done by comparing the GC retention times of expected products with those of standard chemicals.

2.6 LIQUID-PHASE BENZOYLATION REACTIONS

Toluene and benzene from Qualigens Fine Chemicals were purified according to the standard procedure [26]. Benzoyl chloride from Merck was used as such. A mixture of toluene and benzoyl chloride in the molar ratio 3.6:1 (toluene: 10 ml, benzoyl chloride: 3 ml) is refluxed at the b.p of the mixture with 0.100 g of the
activated catalyst sample for 30 minutes. The products were analysed using gas chromatography. (Chemito 8510, SE 30 column, FID detector, N₂ carrier gas, injection port temperature 250°C, column temperature programmed as 100°C for 2 minutes followed by heating at the rate 7° per minute upto 170°C, detector temperature 250°C). The products were identified by GC – MS.

Similarly a mixture of benzene and benzoyl chloride in the molar ratio 4.3:1 (benzene: 10 ml and benzoyl chloride : 3 ml) is refluxed at the boiling point of the mixture with 0.150 g of the activated catalyst sample for 1.5 hours. The products were analysed using gas chromatography, with details the same as for the previous benzoylation.
Fig. 2.4.1 Reactor set-up for reactions carried out at atmospheric pressure
REFERENCES

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