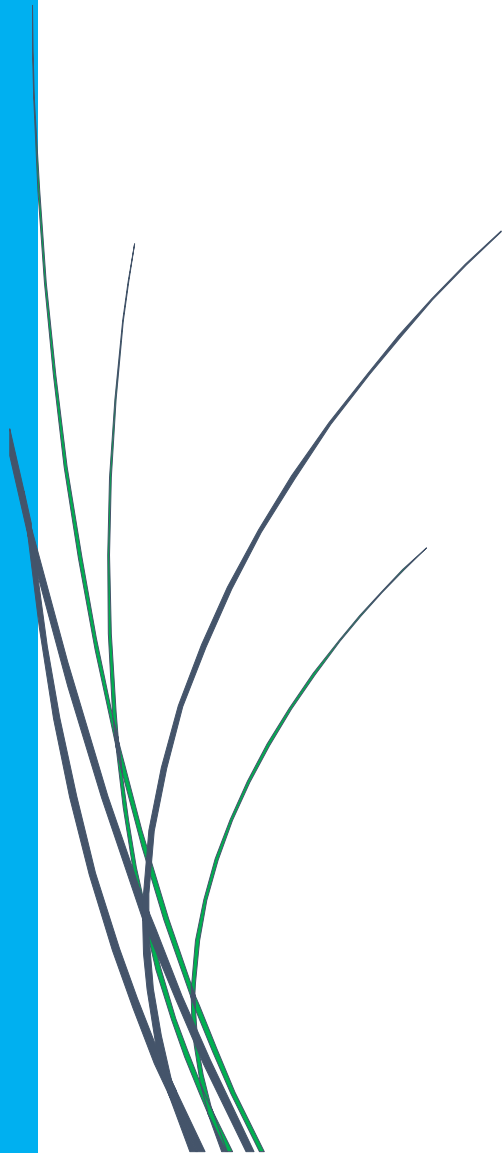




## Chapter:2

# **Experimental methods and characterization**





## 2.1 Introduction

This section deals with the experimental techniques used in the present study for the preparation, characterization, and screening of catalysts for the ESR reactions. It also includes different components of fabricated experimental set up to investigate the performance of synthesised catalysts. Thorough characterization of the catalysts was performed to correlate specific physico-chemical properties to their activity and product selectivity.

## 2.2 Catalyst preparation

The co-precipitation and wet impregnation methods were used for preparation of most of the catalysts. The nano-casting approach was also used for reformulation of catalysts from the deactivated catalysts. The novel solvothermal route of catalyst preparation was used for nano-cube shaped catalyst preparation. First time a novel route of catalyst preparation was also discovered and it was termed solvothermal precipitation.

## 2.3 Catalysts Characterization

**Table 2.1** Properties of catalyst and characterization techniques

Properties of prepared catalyst	Techniques
Surface area	N <sub>2</sub> physisorption
Crystallite size and phase	Powder X-ray diffraction
Pre-reduce temperature	Temperature-programmed reduction (TPR) with H <sub>2</sub>
Morphology	Scanning Electron Microscopy
Particle size analysis	Transmission electron Microscopy
Functional group analysis	ATR-FTIR
Oxidation states	X-ray photoelectron spectroscopy

### 2.3.1 Surface area

The specific surface area was analyzed by Smart Sorb 92/93 surface area analyser using nitrogen physisorption at liquid nitrogen temperature. Prior to perform the analysis catalyst was degassed at 573K for 3h to remove the adsorbed atmospheric gases. In case of the metallic state of active metals, degassing was performed in inert atmosphere at aforementioned temperature for specified time duration.

### 2.3.2 XRD

The high-resolution X-ray powder diffraction (HR-XRD) patterns were collected by using RIGAKU SMART Lab diffractometer operating at 45 kV and 200mA and equipped with monochromator Cu K $\alpha$  ( $\lambda=0.154\text{nm}$ ). The Scan resolution and scan speed were kept 0.0002 and 4.0627 degree/min respectively. The data were recorded in  $2\theta$  values between  $10^\circ$  to  $80^\circ$ , at a step width of  $0.02^\circ$  and with scan rate of  $4.0^\circ/\text{min}$ . The crystalline phase analysis and crystallite size calculation were performed by the data obtained from X-ray diffraction patterns of catalysts. The Rietveld refinement was performed by using Fullprof software to confirm the phases, crystallite size calculation and crystal structure file generation (.cif). The crystal structures were drawn with the help of Vesta software.

### 2.3.3 TPR

The Temperature programmed reduction (TPR) were performed to find out the temperature of pre-reduction and different reducible species present in calcined catalysts. The U-shaped quartz reactor was used to perform the reaction. Prior to start the experiment, the catalyst was outgassed at 573K for 1 h. On cooling back to room temperature, the sample was heated up to 1173K at the rate of 15 K per minute in the 5% H<sub>2</sub> with Ar atmosphere. The consumption of hydrogen was analysed by thermal conductivity detector (TCD).

### 2.3.4 TGA

The Thermogravimetric analysis (TGA)-Differential scanning calorimetry (DSC) is an analytical method of thermal analysis used to measure the mass transformation as a function of temperature (at constant heating rate) or time (at constant temperature and mass loss). In this work, the TGA is used to find out the calcination temperature of the precipitate obtained during catalyst preparation. The measurement is carried out in presence of air or in inert atmosphere (helium or argon) and mass change is recorded as a function of temperature increase. As sample is heated, it can lose weight by drying or release of various gases.

TGA was performed on Perkin Elmer Pyris 1 model in oxidative atmosphere of mixture of air and inert gas. Maximum temperature was chosen for stability of sample implies the completion of all chemical reactions. The sample starts heating with the rate of 20 °C/min starting from 40 °C to 1000 °C temperature range. Resulting curve obtained was steeper with close onset temperature.

### 2.3.5 FTIR

ATR-FTIR (Attenuated Total Reflectance- Fourier Transform Infrared Spectroscopy) measurements were carried out at room temperature on a Bruker Eco-ATR Alfa FT-IR spectrometer equipped with ZnSe attenuated total reflection (ATR) accessory. All spectra were taken in resolution of 4 cm<sup>-1</sup> with 60 scans and reproducibility of 0.01 cm<sup>-1</sup>.

### 2.3.6 Imaging techniques

Morphology and particle size of catalysts were studied by using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). The morphology of nano particle catalysts were analysed with high resolution scanning electron microscope (HR-SEM) equipped with Energy

dispersive analysis of X-Ray (EDAX) of company FEI™ NOVA NANO SEM 450 and AMETEK respectively. The Transmission electron microscope (TEM) analysis were performed with FEI™ TECNAI G2. The high resolution TEM image and selected area diffraction pattern (SAED) were also recorded. The Energy Dispersive X-Ray Spectroscopy (EDS) was also performed for elemental analysis of synthesized catalyst. The inter-planer distance and the particle size of synthesized catalyst were calculated with the help of image J software. The AFM was performed (Bruker NanoDrive) in peak force tapping mode with antimony doped Si tip having frequency 75 kHz.

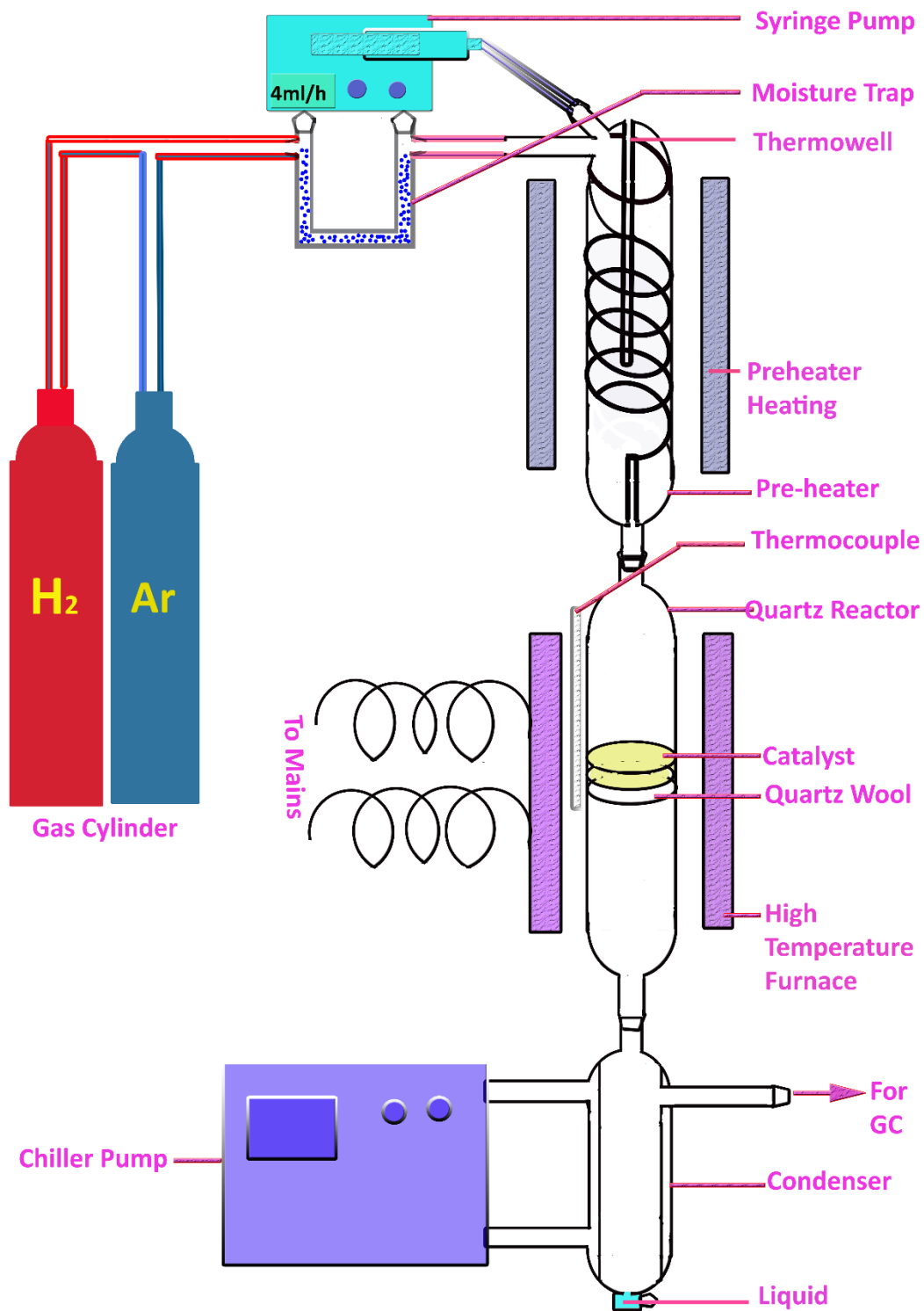
### 2.3.7 XPS

The oxidation states of element present in catalysts were analysed by X-ray photoelectron spectroscopy (XPS). These were performed by (AMICUS, Kratos Analytical, A Shimadzu Group Company) using monochromated Mg K $\alpha$  (1253.6 eV) source.

### 2.4 Fabrication of experimental set up to investigate the catalyst activity

The assembled experimental set up can be divided into following sections:

- I. Feeding section
- II. Preheater and reactor section
- III. Products condensing-separating system
- IV. Reactants and products analysis system



**Figure2.1** Schematic diagram of complete set up designed to perform ESR.

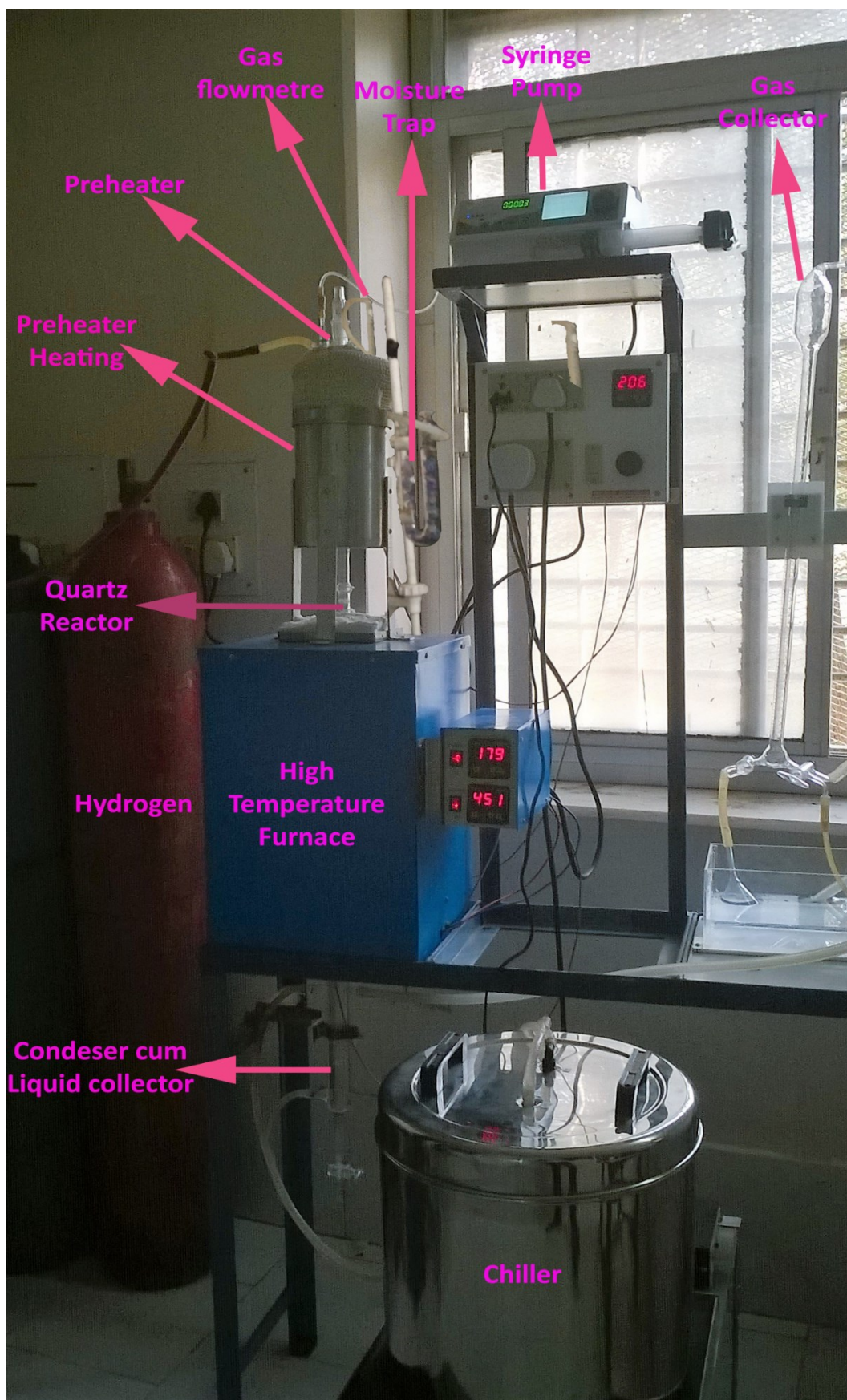


Figure 2.2 Designed set up to perform ESR.



- I. Feeding section: This section consists of two types of feeding gas and liquid. The gas bubble flow meter was used to measure the flow rate of outlet and inlet gas. Prior to the gas feed into the preheater section, the U- shaped moisture trap filled with silica gel was assembled so that even small amount of moisture gets trapped.
  - i. Gas feeding: The feeding of Ar and H<sub>2</sub> were used to create the inert atmosphere and pre-reduction of catalyst respectively inside the reactor system. It was fed with the help of pressurized cylinder.
  - ii. Liquid feeding: liquid mixture was fed by syringe pump MM810 The syringe pump has mechanical and rate accuracy  $\pm 2\%$  and  $\pm 3\%$  respectively. The syringe having maximum volume of 50ml was used to feed the mixture in preheater region.
- II. Preheater and reactor section: The preheater region was designed with cone and socket joint in a way so that ahead of it, reactor can be fitted easily. The temperature was controlled by covering preheater with thermoflex assembled with microprocessor cum temperature controller. The designed preheater has thermowell region to control the temperature during operation.

The reactor was designed as per reaction requirements and fabricated by the quartz material to operate at higher temperature. The reactor was designed in a way so that the temperature at the bed of the catalyst can be monitored during reaction. The reactor was kept in vertical furnace controlled by microprocessor cum temperature controller.
- III. Products condensing-separating system: This section contains condenser cum liquid collector equipped with refrigerated cold water circulating system. The condenser was fabricated by quartz material as per requirement of liquid

collection with gaseous outlet. To maintain lower temperature (270-271K), the temperature of condenser was controlled by circulating the water by refrigerated cold water circulating system.

- IV. Reactants and products analysis system: The reactants concentration and product was analysed with Thermoscientific Gas Chromatogram (TRACE 1110) equipped with TCD and FID with methanator. The Porapak Q column (80-100 mesh size) was used for the analysis of liquid mixture residue and gaseous hydrocarbon mixture (CO, CO<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>). Hydrogen gas was analyzed in Molecular sieve column. For the reproducibility of data five times data was collected and average value was taken for further calculation.

$$H_2 \text{ yield (\%)} = \frac{\text{moles of } H_2 \text{ produced by ESR}}{\text{moles of ethanol fed} \times 6} \times 100 \quad (2.1)$$

$$X_{\text{reactant}} (\%) = \frac{F_{\text{reactant in}} - F_{\text{reactant out}}}{F_{\text{reactant in}}} \times 100 \quad (2.2)$$

$$\text{Selectivity of product } Y (\%) = \frac{N \times \text{moles of } Y \text{ produced}}{2 \times \text{moles of ethanol converted}} \times 100 \quad (2.3)$$

Selectivity of H<sub>2</sub> (%)

$$= \frac{N \times \text{moles of } H_2 \text{ produced}}{[3 \times (F_{\text{ethanol in}} - F_{\text{ethanol out}}) + (F_{\text{water in}} - F_{\text{water out}})]} \times 100 \quad (2.4)$$

Where,  $F_{\text{reactant in}}$  and  $F_{\text{reactant out}}$  are the molar flow rate of the species at the inlet and the outlet of the reactor, respectively. N is the stoichiometric factor between the carbon-containing products and ethanol.