CHAPTER 3

3. MATERIALS AND METHOD:

This work is concerned with the synthesis and characterization of nano-composite fibers suitable for use as catalyst in water gas shift reaction. Effort has been made to prepare copper oxide/cerium oxide (CuO/CeO_2) nanofibers for this purpose. CuO/CeO_2 composites nanofiber in various compositions have been prepared and tested for their catalyst activity, morphology, surface characteristics and thermal stability. The details of the chemicals and materials used and procedures employed are given in the following sections.

3.1. MATERIALS:

3.1.1. Chemicals and gases:

Following chemicals and gases were used for preparing copper loaded ceria nanofibers for use as catalysts in water gas shift reaction. Their qualities together with the name of manufacturer/ suppliers are given in Table 3.1. All chemicals and gases were used as received.

Table 3.1 Chemicals used in the study

S. No.	Chemicals and gases	Manufacturer/ Suppliers	Quality
1	Cerium nitrate hexa-hydrate(CN)	Sigma-Aldrich, Germany	99% pure, AR
2	Copper acetate monohydrate(CA)	Sigma-Aldrich, Germany	≥99% pure, AR
3	Polyvinylpyrrolidone(PVP)	Sigma-Aldrich, USA	MW=$1.3x10^6$gm/mol
4	Ethanol	E. Merck, Germany	99% pure, AR
5	Acetic acid	E. Merck, Germany	99% pure, AR

6	Carbon monoxide	Biotex scientific company	999.% Pure
7	Nitrogen	Sapana Enterprises, Varanasi	99.9% Pure
8	Argon	Sapana Enterprises, Varanasi	99.9% Pure
9	Hydrogen	Hardware & machine, Varanasi	99.9% Pure

3.1.2. Equipments:

List of various equipment and their auxiliary units are given in Table 3.2.

Table 3.2 List of equipments used in the study

S.N.	**Equipment**	**Make and Model**	**Specification**
1	High Voltage power supply	Goldstar, New Delhi, India	0-40KV
2	Syringe pump	AYRA N801 New era pumps, USA	1-99ml/min
3	Gas chromatography	NUCON 5765 New Delhi, India.	Microprocessor Temperature Controller with Multi Ramp Temperature Programming,
4	Needle	SGE, Austrailia	Feed rate upto1.0ml
5	SEM	Zeiss EVO 18, UK	Magnification-1000X, voltage- 15kV

6	XRD	Rigaku Ultima IVX-ray diffractometer (Germany)	Cu-Kα radiation at 40 kV and 40 mA.
7	XPS	AMICUS, Kratos Analytical Ltd.	Voltage- 15kV, Current- 12mA.
8	FTIR	Shimadzu 8400	Wavelength range- 400-4000 cm^{-1}
9	BET	Micromeritics ASAP 2020, USA	STD pressure range= 0.05–0.30P/P_0.
10	TGA	Otis mettler thermo-analyzer	Heating rate- 10ºC/min.
11	EDX	Zeiss EVO 18, UK	Voltage of 15kV

3.2. PROCEDURE:

3.2.1. Nanofiber and their Preparation:

Several methods have been developed for preparing nanofibers. Out of these, template syntheses (Li et al; 2006), self-assembly (Yang et al; 2007; Feng et al; 2006), phase separation (Ma et al; 1999), melt-blown (Ellison et al; 2007), and electrospinning (Gu et al; 2007; Panda et al; 2007) are more popular. However, each process presents several challenges. The choice of a process for producing nanofibers depends on the raw materials, fiber alignment, production rate and process cost. In this respect, the electrospinning process has received the most attention due to its capability to produce nanofibers with different materials. The electrospinning process is straightforward and is capable of producing very fine fibers from polymer solutions or from melts with the use of electrostatic force. Currently, it is the most common technique for producing nanofibers of wide range of diameters.

3.2.2. Electrospinning:

The combination of electrospinning with conventional sol-gel process makes it a versatile technique for producing ceramic nanofibers of solid, porous, or hollow structure. Electrospinning process is being used for producing one-dimensional (1D) nanostructures on industrial scale such as nanofibers with controllable diameters, compositions, and morphologies.

3.2.3. Parameters Affecting of Electrospinning Process:

The electrospinning process is governed by several parameters such as casting solution, composition and constituents operating process parameters, and ambient conditions. Solution properties include viscosity, conductivity, concentration, molecular weight, and surface tension. Process parameters include applied electric field, tip to collector distance and cast solution flow rate. Each one of these parameters significantly affects the fiber morphology. Through proper manipulation of these parameters, one can get nanofibers of desired type (Dai et al; 2011). In addition to these parameters, ambient parameters such as humidity and temperature of the surroundings also hold crucial role in determining the morphology and diameter of electrospun nanofibers (Li et al; 2011).

3.2.3.1. Physico-chemical Parameters:

(a) Concentration:

For fiber formation to take place, a particular solution concentration is required. It has been found that at low solution concentration (<0.5% w/v), a mixture of beads and fibers is obtained and as the solution concentration increases the shape of the beads changes from spherical to spindle-form and finally uniform fibers with increased diameters are formed because of the higher viscous resistance (Gu et al; 2008, Li et al; 2003; Lotus et al; 2010). Surface tension and viscosity of solution also play important roles in determining the range of concentrations (0.5 - 30% w/v) from which continuous fibers can be obtained. There should be an optimum solution concentration for the electrospinning process. It is because, at low concentrations beads are formed instead of fibers, whereas, the formation of continuous fibers is affected at high concentrations owing to the inability to maintain adequate flow of the solution at the tip of the needle.

(b) Molecular Weight of Polymer:

Molecular weight of the polymer has a significant effect on rheological and electrical properties such as viscosity, surface tension, conductivity and dielectric strength (Souza et al; 2007). Generally, high molecular weight (250–9.0×10^6g/mol)polymer solutions have been used in electrospinning as they provide the desired viscosity for the fiber formation (Koski et al; 2004). It has been observed that the solution in a polymer of too low a molecular weight tends to form beads rather than fibers, and a high molecular weight polymer solution gives fibers with larger average diameters. The molecular weight of the polymer controls the viscosity of the solution. Also, the chain entanglement plays an important role in the processing of electrospinning (Zhao et al; 2006).

(c) Viscosity:

Viscosity of casting solution plays an important role in determining the fiber size and morphology during spinning of polymeric fibers. It has been found that with very low viscosity continuous fiber formation does not take place and with very high viscosity there is difficulty in the ejection of jet of polymer solution from the needle tip. Therefore, there is a requirement of an optimal viscosity (49-69 poise) for nanofibre formation using electrospinning process (Yang et al; 2007). For solution of low viscosities, surface tension becomes the dominant factor. An increase in the solution viscosity or concentration gives rise to a larger and more uniform fiber diameter (Gu et al; 2008).

(d) Surface Tension:

Surface tension, more likely to be a function of solvent composition in the solution, plays a critical role in the electrospinning process. The formation of droplets, bead and fibers depends on the surface tension of solution. By reducing the surface tension of a nanofiber solution, fibers can be obtained without beads. Generally, the high surface tension of a solution inhibits the electrospinning process because of instability of the jets and the generation of sprayed droplets (Formo et al; 2009). A lower surface tension of the spinning solution helps in electrospinning to occur at a lower electric field.

3.2.3.2. Process Parameters:

(a) Applied Voltage:

The fiber formation occurs only after the attainment of a threshold voltage (0 to 40 kV). This induces the necessary charges on the solution along with electric field and initiates the electrospinning process. In most cases, a higher voltage causes greater stretching of the solution due to the larger columbic forces on the jet as well as a resultant strong electric field. These effects lead to reduction in the fiber diameter and rapid evaporation of solvent from the fibers. Though, the voltage influences the fiber diameter, the extent of its effect varies with the polymer solution concentration and distance between the injection tip and the collector plate (Formo et al; 2009).

(b) Feed Rate:

The flow rate of the polymer from the syringe is an important process parameter as it influences the jet velocity and the material transfer rate. A lower feed rate is more desirable as the solvent will get enough time for evaporation (Mai et al; 2010). There should always be a minimum flow rate of the spinning solution. The high flow rates result in beaded fibers due to unavailability of proper drying time prior to reaching the collector. The optimum flow rate of polymeric sol for the formation of nanofibre catalyst ranged from 0.5-1.5 ml/h.

(c) Type of Collectors:

One important aspect of the electrospinning process is the type of collector used. In this process, a collector serves as a conductive substrate where the nanofibers are collected. Generally, aluminum foil is used as the collector but due to difficulty in transferring the collected fibers and the need for aligned fibers for various applications, other collectors such as, conductive paper, conductive cloth, wire mesh, parallel or grided bars, rotating rod or rotating wheel are also used (Song et al; 2008).

(d) Tip to Collector Distance:

The distance between the tip and the collector has been used as another parameter to control the fiber diameters and morphology. It has been found that a minimum distance is required to give sufficient time to fibers to dry before reaching the collector, with distances that are either too close or too far; beads have been observed (Li et al; 2011).

3.2.3.3. Ambient Parameters:

Apart from solution and processing parameters, ambient parameters such as humidity, temperature, and wind motion affect fiber morphology. It has been found that with an increase in the temperature, there is a decrease in fiber diameter, due to the decrease in the viscosity of the casting solutions. Also, at very low humidity, a volatile solvent may dry rapidly as the evaporation of the solvent is high. Sometimes, the evaporation rate is fast compared to the release of the solution from the tip of the needle, which creates problem with electrospinning. As a result, the electrospinning process may be carried out only for a few minutes before the needle tip gets clogged (Ding et al; 2009). It has also been suggested that the high humidity can help in quicker discharge of the electrospun fibers.

3.3. Preparation of Nanofibers:

In order to generate well-controlled and high-quality ceramic nanofibers by electrospinning, one has to use the following procedure: (1) Preparation of a sol with suitable inorganic precursor and mixing the inorganic sol with a polymer solution to get the right rheology for electrospinning, (2) Electrospinning of the solution to obtain inorganic/organic composite fibers under appropriate conditions, and (3) Calcination of the as-prepared composite fibers in air to yield pure metal oxide fibers. One of the attractive features associated with this method is that the nanofiber mats thus prepared possess high surface areas and small pore sizes (Wang et al; 2006).

3.3.1. The Electrospinning Solution:

It is possible to obtain ceramic nanofibers by directly electro-spinning a sol solution that only contains an inorganic precursor (metal alkoxides or metal salts) and a solvent. Notable examples include CeO_2 (Yang et al; 2005; Qizheng et al; 2008; Xu et al; 2011; Tang et al; 2012; Hwang et al; 2011), SiO_2 (Zhang et al; 2010), Co_3O_4 (Chuangchote et al; 2009), TiO_2 (Ramakrishna et al; 2006), $LiCoO_2$ (Oehmen et al; 2006) and Al_2O_3/ZnO (Baeyens et al; 1996) nanofibers. However, the inappropriate rheological properties and the rapid hydrolysis rates of metal alkoxides or metal salts make it very hard to control the electrospinning process. To solve these problems, one has to introduce a polymer into the solution as a matrix to adjust the rheological properties as well as an additive to act as a catalyst, to control the hydrolysis rate of the precursor (Baeyens et al; 1996).

A typical spinnable precursor solution should contain an alkoxide or metal salt precursor, a polymer, an additive, and a relatively more volatile solvent such as ethanol, water, isopropanol, chloroform, and dimethyl-formamide (DMF). Some catalysts are usually added into the solution to stabilize the precursor and facilitate the electrospinning process. Although only a small amount is required, these additives play an important role in stabilizing the solution as well as the jet. A catalyst such as acetic or hydrochloric, or propionic acid can be used to adjust both the hydrolysis and gelation rates preventing the solution from blocking the needle mouth and thus ensuring a continuous fiber formation (Wang et al; 2006).

In the present work, a casting solution comprising required precursors (cerium nitrate hexahydrate and copper acetate monohydrate), PVP polymer, glacial acitic acid (3-4 drops) and a solvent (ethanol and water) was prepared and used for preparing the green nano-fibers through electrospinning process. The details of procedure used for preparing the casting solution and green nanofibers are discussed below.

3.3.2 The Precursor and Polymer solution:

Cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$) and cupric acetate monohydrate ($Cu(CH_3COO)_2.H_2O$); precursors were used as received. Polyvinyl pyrrolidone (PVP) was used as the base polymer because it has a remarkably large molecular weight and high solubility in the polar solvents. Ethanol and de-ionized water were selected as the solvent and co-solvent, respectively (Li et al; 2011). Aqueous solutions with 0, 10, 20, 30, 40, 50 and 60 mol. % Cu were prepared by dissolving appropriate amounts of $Cu(CH_3COO)_2.H_2O$ in a solution of 0.434 g cerium nitrate hexahydrate prepared in 4 ml of deionized water and kept in seven different vials. In another set of five vials 10% (w/v) solution of PVP in 8 ml ethanol was prepared by adding appropriate amount of PVP and stirring with magnetic stirrer to ensure complete dissolution. For preparing the spinning solution the contents of the first set of seven vials were added separately to the vials containing ethanol solution of PVP. The contents of the vials were mixed together and acetic acid was added drop-wise (2-3 drops) to each vial to get the final solution. The mixed solutions were magnetically stirred for 3 hours at room temperature to form a homogeneous solution.

3.3.3. The Electrospinning Setup:

In 1934, a process was patented by Formhals, wherein an experimental setup was outlined for the production of polymer filaments using electrostatic force. When used to spin fibers this way, the process is termed as electrospinning (Jesse et al; 2006). Electrospinning is a simple method that has attracted enormous attention due to its versatility, ease of use and capability to produce continuous nanofibers. Since 2002, electrospinning has been further explored as a high efficiency method for the generation of 1D ceramic nanofibers (Chong et al; 2007). In the generic design, an electrospinning setup consists of a high-voltage power supply, a spinneret or (a metallic needle), an electrically conductive collector (a piece of aluminium foil or silicon wafer) and a syringe pump. The solution for spinning is loaded in a plastic syringe, which is connected to the metallic needle. In order to control the quality of electrospun fibers, the syringe is often connected to a syringe pump so that a constant and adjustable flow rate of the solution could be maintained. For some experiments, especially for electrospinning of ceramic nanofibers, the setup needs to be placed in a closed box so that the humidity can be varied in a controllable fashion. Depending on the end use of resultant fibers, the collector can be constructed from various materials and in various configurations. Electrospinning is normally conducted under atmosphere conditions (Li et al; 2004).

The electrospinning system continuously used consisted of a high voltage (10-40kv) power supply of 40 kV, a syringe pump a metallic needle and an electrically conductive collector plate. The electrospinning setup is schematically shown in Figure 3.1 and photograph of the assembled setup is given in Figure. 3.2.

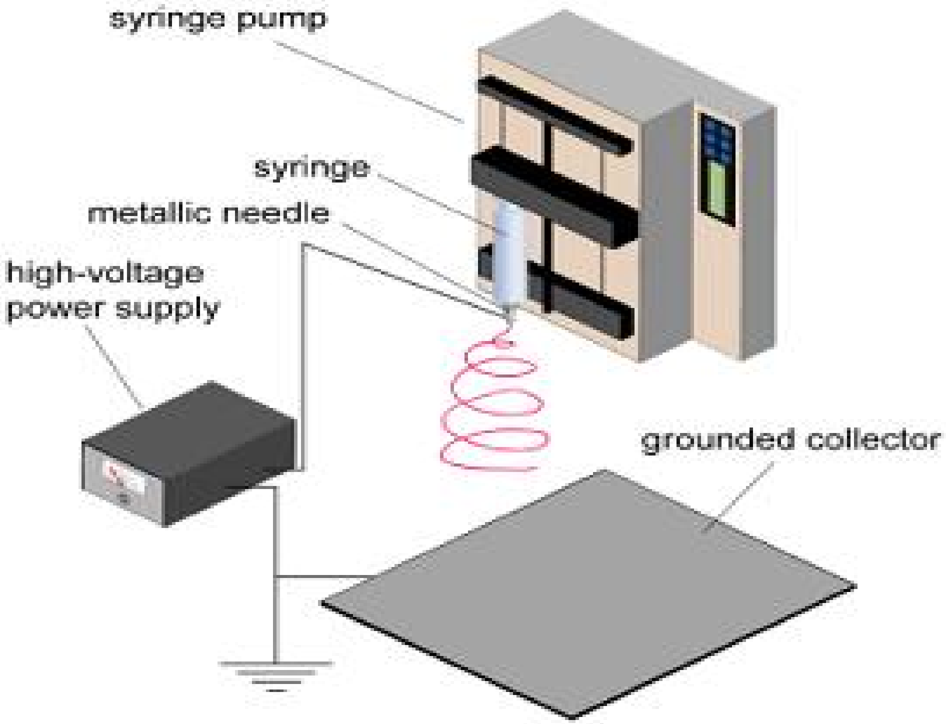

Figure 3.1 Schematic Diagram of the Electrospinning Process

Figure 3.2 Photograph of the Electrospinning Setup

3.3.4. Electrospinning of Composite Nanofibers:

The polymer based sol-gel solution or spinning solution was immediately loaded into a 5ml plastic syringe. A blunt ended 20-gauge stainless steel needle was used as the nozzle equipped with the syringe which was attached with the syringe pump. The positive electrode from a high voltage power supply capable of generating DC voltages up to 40 kV was then attached to the needle and its negative electrode was connected to the collecting plate covered with an aluminum foil. The ground electrode from the same power supply was attached to a piece of flat aluminum foil which was used as the collector plate and placed 10 cm below the tip of the needle to collect the nanofibers. The electrospinning process was conducted in ambient air at room temperature (25±2^{0}C) with the relative humidity of 65±5%. A constant solution feeding rate of 1 ml/h regulated with the help of a syringe pump ensured the steady deposition of nanofibers on the collector plate. In this experiment, a positive high voltage of 18 kV was applied across the needle and the collector plate due to which a fluid jet was ejected from the nozzle. As the accelerated jet moved towards the collector, the solvent evaporated, leaving only ultra thin fibers on the collector plate. The process was continued until all the solution in the syringe was used up. The entire sequence is schematically shown in Figure. 3.3.

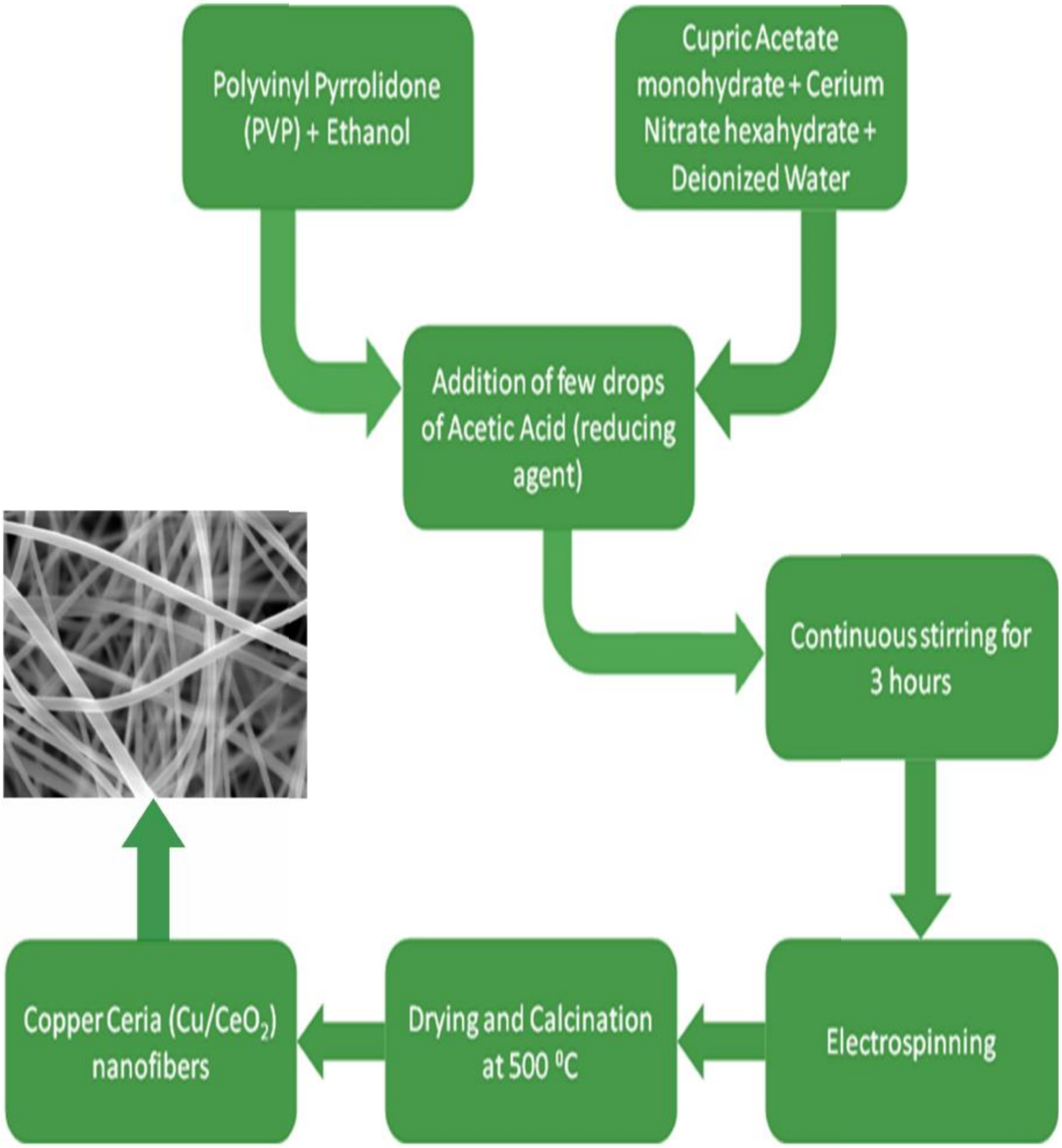

Figure 3.3 Process Flowchart for the Preparation of Nanofibers by Electrospinning Method

3.3.5. Calcinations of Green Nanofibers:

To complete the formation of CuO/CeO_2 nanofibers, the composite fibers prepared as above were left exposed to ambient moisture for 5 hr to allow complete hydrolysis, then electrospun polyvinyl pyrrolidone (PVP) /cerium nitrate hexa-hydrate (CN)/copper acetate monohydrate (CA) fiber mats were removed from the aluminium foil. These composite fibers were placed on a ceramic crucible (which can withstand at high temperature) and consequently calcined at 500^0C in a muffle furnace in presence of air for 3 hr in order to eliminate the organic components and to activate the crystallization of Cu-Ce oxide ($CuO-CeO_2$). The compositions showing various catalysts and their details are given in Table 3.3.

Table 3.3 Types of catalyst prepared and their conditions

Materials	Method of preparation	Components	Decomposition Temp. / Envt.
CeO_2	Electrospinning method	Ce	500^oC/Air
10% CuO/CeO_2	Electrospinning method	Cu-Ce	500^oC/Air
20% CuO/CeO_2	Electrospinning method	Cu-Ce	500^oC/Air
30% CuO/CeO_2	Electrospinning method	Cu-Ce	500^oC/Air
40% CuO/CeO_2	Electrospinning method	Cu-Ce	500^oC/Air
50% CuO/CeO_2	Electrospinning method	Cu-Ce	500^oC/Air
60% CuO/CeO_2	Electrospinning method	Cu-Ce	500^oC/Air

3.4. Characterization of Green and Calcined Cu-Ce Oxide Nanofibers:

3.4.1. X-Ray Diffraction (XRD):

Rigaku Ultima IV wide-angle X-ray diffractometer (Germany) with a graphite mono-chromator was used for performing X-ray diffraction using Cu-Kα source with a wavelength of 0.154 nm. The generator was operated at 40 kV and 20mA. The required amount of nanofibres were placed on the silica sample holder at room temperature (~ 25°C) and were scanned at the diffraction angle 2θ from 10° to 80° and scanning rate of $2°min^{-1}$. The XRD peak width at half maxima was used to determine the crystallite size as per Scherrer formula:

$$D = \frac{K^{a}}{\left(Cos^{-}\right)} \qquad (3.1)$$

Where, K = 0.9, (X-ray wavelength) λ = 0.154 nm, β is full width at half maximum and θ is the Bragg's diffraction angle. The percentage crystalline of NFs and NF composites was determined from the ratio of crystalline area to the total area using the following expression:

$$\%\,\text{Crystallinity} = \frac{A_c}{A_c + A_a} \times 100\,, \qquad (3.2)$$

Where, A_c are A_a are areas of crystalline and amorphous components, respectively.

3.4.2. Brunauer Emmett Teller (BET) Surface Area:

The BET surface area of the samples were analyzed by nitrogen adsorption–desorption isotherm measurements at 77 K on an adsorption apparatus (ASAP 2020, Micromeritics Instruments, USA). The fiber samples were degassed at room temperature for 24 hours prior to actual measurements. The BET specific surface area was determined by the multipoint BET method using the adsorption data in the relative pressure (P/P_o) range of 0.01-0.99 and 0.05-0.3 for particles and fiber samples, respectively.

3.4.3. Fourier Transforms Infrared (FTIR) Spectroscopy:

The FTIR measurements were performed in transmittance mode at room temperature from 400 to 4000 cm^{-1} using Shimadzu 8400, USA with a resolution of 4 cm^{-1}. nanofibres spectra were recorded by making pellets with 10 % particles in KBr powder and direct spectra was taken for nanofibres samples.

3.4.4. Morphological Investigation:

The morphology of the electrospun polymer nanofibers and foam scaffold were examined using a high resolution Scanning Electron Microscope (Zeiss EVO 18) by operating at an accelerating voltage of 2-5 kV. Based on the SEM micrographs, fiber diameters were determined using an image visualization software Image-J developed by the Upper Austria University of Applied Sciences.

3.4.5. X-Ray Photoelectron Spectroscopy (XPS) Analysis:

The XPS measurements were made using an ultrahigh vacuum AMICUS photoelectron spectrometer equipped with Mg-K_α X-ray for primary excitation and KRATOS VISION 2 software. All the samples were analyzed in triplicate for error free area fitting. All binding energy (BE) values reported in the present work are with reference to carbon C 1s core level at 284.6 eV. The curve fitting of the high resolution spectra were performed with combined Gaussian-Lorentzian functions.

3.4.6. Thermo Gravimetric Analysis (TGA):

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on an Otis Mettler Thermo Analyzer in air atmosphere, at a heating rate of 10°C/min.

3.4.7. Energy Dispersive X-Ray Spectroscopy (EDX):

The EDX were recorded on Zeiss EVO 18 scanning electron microscope (SEM) instrument. An accelerating voltage of 15kV was applied and a magnification of 1000X was used.

3.5. The Catalytic Activity of Cu-Ce Oxide Nanofibers:

3.5.1. Reactor:

A fixed bed tubular flow reactor was chosen for the present study. The reactor consisted of two co-axial corning glass tubes of 20 mm and 50 mm diameter. A helical coil of glass tube placed in between the co-axial tubes served as a preheater for the reactants. Figure 3.4 shows the detailed dimensions of the reactor. There is a hole in the lower part of the outer tube, to prevent breakage of reactor due to the expansion or contraction of air in between co-axial tubes as the unit is subjected to the variation of temperature from ambient to the reaction temperature. The pre-heated gaseous reactants enter the catalyst bed, kept in the inner tube. The product stream from the bottom of the reactor is cooled in a condenser to the ambient condition and then sent for GC analysis.

The reactor was mounted vertically. The down flow mode of stream of reactants was used to avoid the distortion of the bed. The catalyst was placed on a thin layer of glass wool which is supported on sintered glass disc inside the inner tube. A thermocouple well made of 4mm diameter glass tube was inserted axially from the bottom all the way to the center of the disc for temperature measurement and control. The heating system for the reactor consisted of a tubular electric furnace. The temperature of the bed was controlled ± 0.5 ^{0}C with the help of a microprocessor controlled temperature controller.

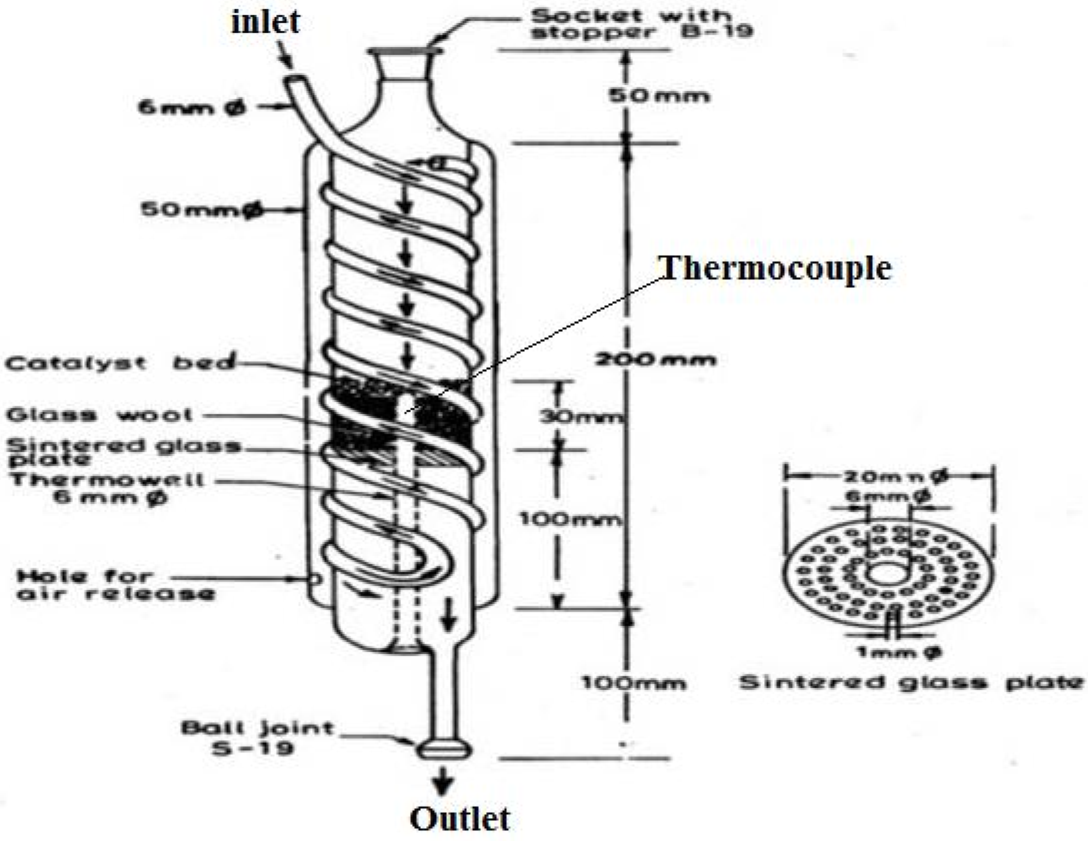

Figure 3.4 Catalytic Reactor

The special feature of the reactor is that the vaporizer, preheater and the reactor are merged together in a single unit. This compact unit not only separates the vaporizer and preheater but also saves electrical energy by avoiding separate furnace for the vaporizer and preheater. The reactor is placed in the furnace in such a manner that the catalytic zone is well within the constant temperature zone.

3.5.2. Activity Measurement:

The experimental setup consisted of following sections: reactants feeding section, reaction section and product cooling and separation section. The schematic diagram of the experimental setup is shown in Figure. 3.5 and its photograph are shown in Figure. 3.6. The feeding system consisted of carbon monoxide and nitrogen cylinders, flow measuring devices; mercury safety device and bubbler. The main reaction section consisted of a compact bench scale tubular reactor, as described above, a tubular furnace and a micro-processor based temperature controller. The last section comprised of product cooling and gas-liquid separating units.

The 50 mg of catalyst was taken and placed over the glass wool layer inside the reactor and maintained at the desired temperature. The carbon monoxide at the flow rate of 1.5ml/min and nitrogen at 58.5 ml/min were mixed together. Nitrogen and CO were fed from respective compressed gas cylinders. The individual gas flow rates were controlled with the help of needle valves and measured with a digital flow meter. A mercury seal was used as a safety device for checking any sudden rise in the gas mixture pressure. A portion of this mixture was bubbled through water pool kept in a vertically mounted burette. To maintain the constant rate of water evaporation, the level of water in the burette was maintained by refilling it with water after vaporization of 1ml of liquid. The decrease in water level in the burette was used to know the amount of water evaporated. On an average, the evaporation rate was maintained at 0.15 ml/min and accordingly the flow of the mixed gases passing through the burette was adjusted. The water vapors loaded gas mixture was then mixed with the dry gas mixture to prepare the reaction mixture and fed to the reactor through the in-built pre-heater for the production of hydrogen. All experiments were carried out at atmospheric pressure and in the temperature range of 150-400 ^{0}C. A J-type thermocouple was inserted into the center of the catalyst bed to monitor the reaction temperature. The catalyst bed temperature was maintained at the desired level with the help of a microprocessor temperature controller. The reaction products from the bottom of the reactor were sent to a condenser and gas-liquid separating assembly kept in an ice-bath to remove water from the mixture before gas-chromatographic analysis. The water free reaction products were analyzed using an on-line gas chromatograph (NUCON-5765). A Porapack Q column, methanizer and FID were used to analyze CO and $CO_2$with nitrogen as the carrier gas. Hydrogen was analyzed using molecular sieve column and TCD with argon as carrier gas.

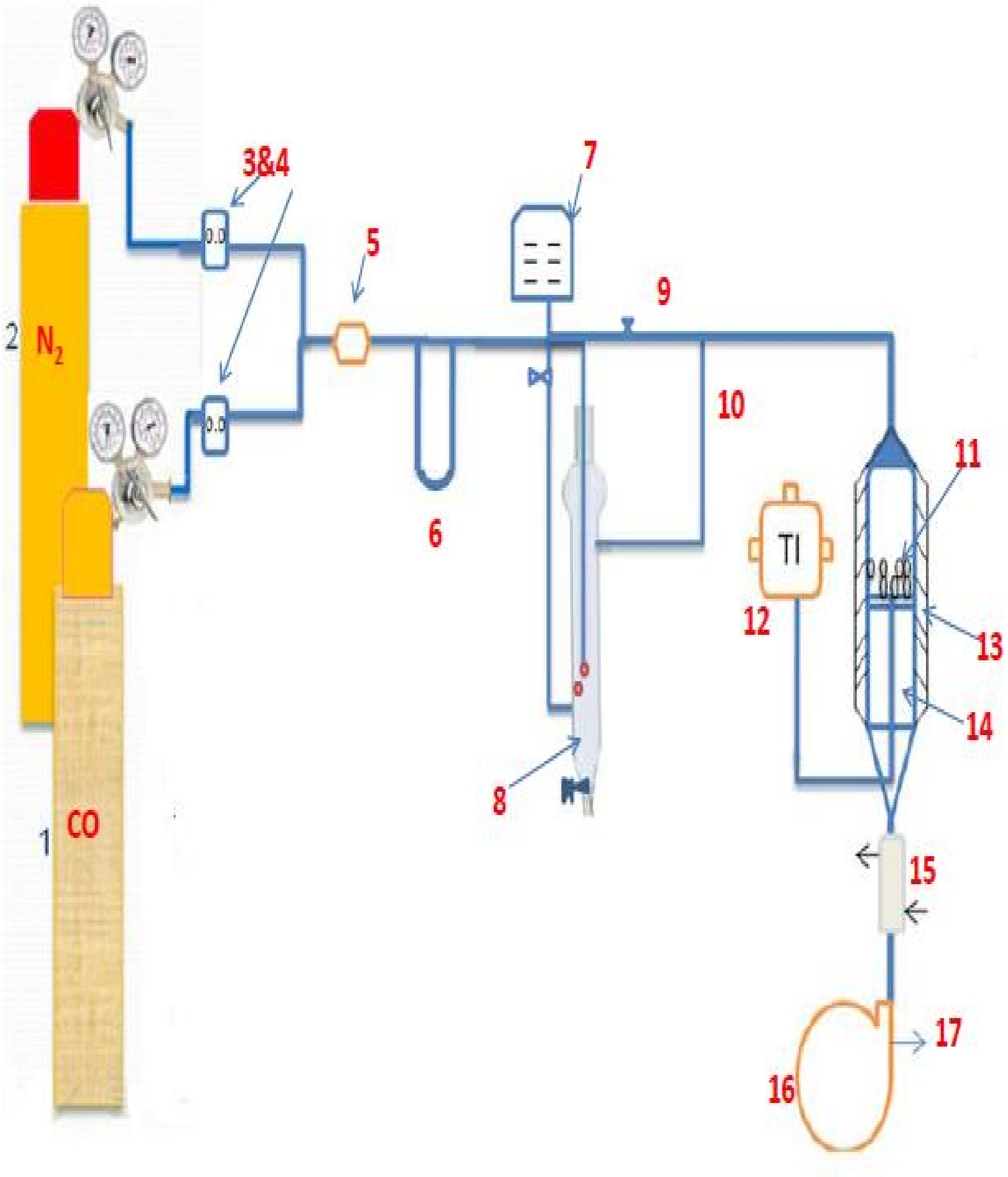

Figure 3.5 Schematic diagram of experimental setup: 1. CO cylinder, 2) N_2 cylinder, 3&4) Gas flow meters, 5) Sampler, 6) Hg safety device, 7) Water reservoir, 8) sparser burette, 9) Primary gas controller, 10) Secondary gas, 11) collector plate,12) Thermocouple and Temperature controller, 13) Tubular furnace, 14) Reactor, 15) Condenser and 16) Gas storage

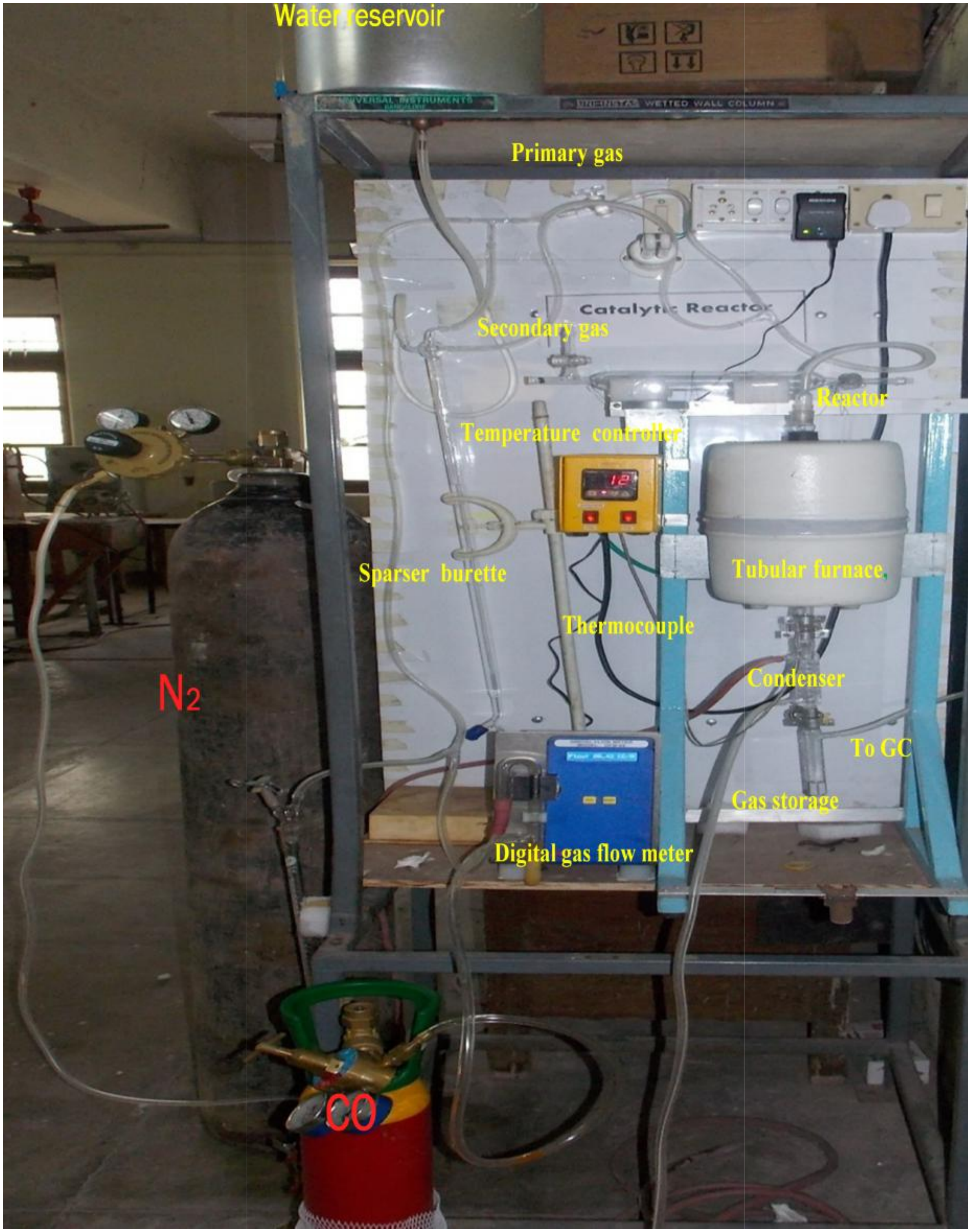

Figure 3.6 General view of experimental setup: 1. CO cylinder, 2) N2 cylinder, 3&4) Gas flow meters, 5) Sampler, 6) Hg safety device, 7) Water reservoir, 8) sparser burette, 9) Primary gas controller, 10) Secondary gas, 11) collector plate, 12) Thermocouple and Temperature controller, 13) Tubular furnace, 14) Reactor, 15) Condenser and 16) Gas storage

The prepared catalyst performance is demonstrated by catalyst activity, H_2 yield (vol %), and H_2 selectivity. The catalyst activity is presented as CO conversion (X_{CO}) and defined as follows:

$$\%\text{CO Conversion} = \frac{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}}{CO_{in}} \text{x} 100 \qquad (3.1)$$

The catalyst performance is demonstrated by catalyst H_2 selectivity it was calculated according the Haryanto et al (2009) then the hydrogen selectivity (SH_2) is defined as follows:

$$Hydrogen\ selectivity = \frac{[\text{H}_2]_{\text{Yield}}}{[\text{H}_2]_{\text{Theoretical}}} X100\% \qquad (3.2)$$

Here, $[H_2]_{\text{maximum}}$ is the maximum H_2 yield based on thermodynamic equilibrium at the different temperature. On the basis of the water gas shift reaction equation 1.14, it can be inferred that H_2 yield (vol %) can be related to CO conversion (X_{CO}) as follows:

$$\text{Hydrogen yield (\%V)} = \frac{X_{CO}}{1+X_{CO}} \qquad (3.3)$$