Chapter 2

Catalyst Preparation Methods, Characterization Techniques and Experimental Framework

2.1 Introduction to Catalysts

A catalyst is a substance that is known to speed up chemical reactions, or lower its energy requirement by reducing the required temperature and/or pressure, without being consumed. They are vital to numerous industrial processes, ranging from the production of bulk chemicals, fine chemicals, and pharmaceuticals to the refinement of petroleum derivatives. Catalysts are also essential for environmental activities like pollution prevention and carbon capture. A catalyst composition, surface area, structure, and active site dispersion all parameters affect its efficiency. It is essential to thoroughly characterize catalysts in addition to ensuring that they are prepared with the greatest possible attributes in order to ensure their effectiveness and durability. [1-4]

This chapter will discuss many processes used to synthesize catalysts as well as the characterization techniques used to assess their structural, chemical, and catalytic qualities. Understanding these processes is necessary for designing and utilizing catalysts in both commercial and experimental contexts. Experimental framework including catalyst preparation, catalyst testing is also discussed for this work.

2.2 Catalyst Preparation Methods

The catalytic properties of any catalyst are strongly affected by the steps involed in the catalyst preparation and its raw material. There are different methods available to synthesize a catalyst. The choice of the catalyst preparation method depends on physical and chemical characteristics required in the catalyst. The preparation method also depends on raw material. Some of the key catalyst preparation methods are discussed below:

2.2.1 Impregnation Method

Among the most popular methods for synthesizing heterogeneous catalysts is the impregnation process. Using this technique, active metal species are deposited onto a support material, usually an inert oxide like titania, silica, or alumina. A metal precursor, such as a metal salt or complex, is first dissolved in a solvent to start the process. The metal precursor is then allowed to diffuse into the support pores by submerging the support material in this solution. Following impregnation, the catalyst undergoes drying to eliminate the solvent, followed by high-temperature calcination to transform the precursor into the active metal phase.

Depending on the precursor and the calcination conditions, the impregnated metal species may be metal hydroxides, metal oxides, or other intermediates. This approach is quite adaptable and easy. The possibility of inadequate metal dispersion, which might result in decreased catalytic activity, is one of its main drawbacks. Additionally, incorrect calcination temperature can result in sintering, or the aggregation of metal particles, which lowers the catalyst effective surface area. [5-8]

There are two kinds of impregnation: *dry and wet*. Incipient impregnation or capillary impregnation are also known as dry impregnation technique. The volume of distilled water is assumed to be equal to the volume of pores in the dry impregnation process. To ensure that the solution is evenly distributed across the support material, the mixture is thoroughly stirred. To get rid of the solvent, the impregnated mixture is then left to dry in an oven. To turn nitrates into oxides, the dried material is stored for calcination in a muffle furnace. The amount of distilled water applied in the wet impregnation process is in excess than the support pore volume. For the salt solution to disperse evenly across the support, the combination of salts needs to be shaken vigorously enough to use more solvent.

Applications: Catalysts for processes including hydrogenation, oxidation, and cracking are frequently prepared by the impregnation process.

Drawback: It is difficult to obtain a large weight% of active component by dry impregnation method.

2.2.2 Precipitation Method

Precipitation involves dissolving a metal precursor (often a salt) in an aqueous solution, followed by the gradual addition of a precipitating agent. To guarantee the development of a solid precipitate, this process usually takes place at controlled temperature and necessitates meticulous control of reaction conditions. The active catalyst is synthesized by filtering, washing, drying, and calcining the precipitate once it has formed.

Although this approach is straightforward and economical, it frequently produces catalysts with small surface areas and little control over the size of the metal particles. Similar to other techniques, calcination may result in phase changes that impact the catalyst functionality. [9-11]

Applications: Making catalysts for oxidation processes, hydrogenation, and catalytic cracking frequently involves precipitation.

Drawback: A broad range of particle sizes is frequently produced by the precipitation process, which may result in irregular catalytic activity. The performance of the catalyst may be impacted by the difficulty of achieving uniform particle size.

2.2.3 Co-precipitation Method

By changing the pH or adding a precipitating agent, two or more metal ions can precipitate from an aqueous solution simultaneously using the co-precipitation method. When a uniform distribution of several metal species is required, this technique is frequently employed. A precipitating agent, like sodium hydroxide or ammonia, is usually added after the metal salts have been dissolved in a solvent to cause the production of solid particles. To get rid of any remaining contaminants, the catalyst is filtered, cleaned, and dried after precipitation. In order to transform the metal precursors into their active forms, the catalyst is lastly calcined at high temperatures. Co-precipitation is frequently used to synthesize catalysts with a consistent metal distribution and enables the manufacture of multi-metallic catalysts. [12,13]

Applications: When synthesizing catalysts for processes such as selective hydrogenation, methanation, and the elimination of nitrogen oxides from exhaust gases, the co-precipitation approach is frequently used.

2.2.4 Sol-Gel Method

The sol-gel method is a chemical procedure that produces catalysts with enormous surface areas and controlled porosity. A liquid precursor, usually metal alkoxides, is transformed into a solid gel-like material by hydrolysis and polymerization processes. The sol-gel method ensures that the active components are dispersed evenly by carefully regulating the structure of the catalyst.

Metal alkoxides are first dissolved in a solvent, and then water and other reagents are added to start the hydrolysis process. The organic components are subsequently eliminated and the required oxide phases are formed by drying and calcining the resultant gel at high temperatures. The sol-gel process is especially helpful for synthesis of catalysts with small particle sizes and large surface areas, both of which are necessary to maximize catalytic activity. [14-16]

Applications: Oxide-based catalysts, as those used in fuel cells, environmental applications, and catalytic oxidation, are frequently prepared using this method.

Drawback: Often including several processes, such as hydrolysis, condensation, aging, and drying, the sol-gel procedure can be time-consuming and necessitates exact control over variables like pH, humidity, and temperature.

2.2.5 Chemical Vapor Deposition (CVD)

The method of introducing gaseous precursors containing the target metal or metal oxide into a reaction chamber is known as chemical vapor deposition, or CVD. When these precursors come into touch with a heated substrate, they break down or react, causing a solid substance to be deposited. Thin films or coatings of active catalyst material are frequently applied to a support surface using CVD.

The ability of CVD to create homogeneous, thin layers of catalyst material with exceptional control over composition and thickness is its primary benefit. The procedure can be used to deposit a variety of materials and can be performed in a number of settings, such as air pressure or low pressure. Nevertheless, CVD is frequently more costly than alternative preparation techniques and calls for specific equipment. [17-18]

Applications: In addition to being utilized extensively in the semiconductor sector, CVD is also employed to prepare catalysts for fuel cells and microreactors.

Drawback: Reaction parameters such as temperature, pressure, gas flow rates, and precursor concentrations have a significant impact on the CVD process. Maintaining ideal conditions is difficult and necessitates careful observation, which complicates the procedure.

2.2.6 Atomic Layer Deposition (ALD)

A highly regulated deposition method called atomic layer deposition (ALD) involves introducing precursor gases into a reaction chamber one after the other. A single atomic layer is deposited on the catalyst surface as a result of each precursor's reaction. ALD is perfect for applications where uniformity and atomic-level control are crucial because it offers exceptional precision in regulating the catalyst material composition and thickness. [19,20]

Applications: High-performance catalysts are created using ALD in fields like fuel cells, nanocatalysis, and catalysis for energy conversion technologies.

Drawback: ALD works by depositing individual atomic layers one after the other, which slows down the deposition process. Because it can result in higher manufacturing costs and longer processing times, this is not the best option for large-scale production.

2.3. Characterization Techniques for Catalysts

To comprehend a catalyst's performance and behavior under reaction conditions, it is crucial to assess its qualities once it has been synthesized. The structure, composition, surface area, and activity of the catalyst are evaluated using a variety of characterization techniques.

2.3.1 X-ray Diffraction (XRD)

One effective method for figuring out a catalyst crystalline structure and phase composition is X-ray diffraction (XRD). A diffraction pattern is produced when X-rays are directed at a sample and are diffracted by the crystalline material lattice planes. The idea behind it is that when X-rays are pointed at a substance, they interact with the atoms that make up the crystal structure. X-rays are diffractionally produced by these interactions, and their analysis can reveal information about the atomic structure of the substance.

The ensuing peaks reveal details on the catalyst phase composition, crystallinity, and crystal size. When it comes to identifying the metal or metal oxide phases in a catalyst and figuring out whether any phase transitions have taken place during production or usage, XRD is especially helpful. The size of crystallites, which may affect the activity of the catalyst, can also be estimated using this method. [21-24]

When an X-ray beam strikes a crystal, the crystal planes disperse the intense radiation. According to Bragg's Law, when X-rays are diffracted at particular angles, constructive interference where waves add up occurs. A diffraction pattern produced by this constructive interference can be utilized to examine the material's atomic arrangement. The Scherrer equation is frequently used in X-ray diffraction (XRD) calculations to determine the crystal size. This formula links the size of the crystallites (or crystallite size) in a material to the widening of X-ray peaks. The Scherrer equation's formula is:

$$D=K\lambda/\beta\cos\theta \tag{2.1}$$

where,

D is the size of the crystallite (in nanometers, nm).

K is the Scherrer constant, which is usually considered to be 0.9 but can vary from 0.9 to 1.0 depending on the crystals form.

λ = X-ray radiation wavelength (in nanometers, nm)

β =The diffraction peak full width at half maximum (FWHM) (in radians) The Bragg angle, expressed in radians, is equal to half of the diffraction angle.

Finding the peaks in the experimental X-ray diffraction (XRD) pattern and comparing them to the standards in the JCPDS/ICDD database are the usual steps in the process of creating a JCPDS (now ICDD) card number using XRD data.

Applications: Catalysts, particularly those employed in procedures requiring exact phase control, like catalytic hydrogenation or cracking, can have their crystalline structures examined using XRD.

2.3.2 Scanning Electron Microscopy (SEM)

Method for examining the composition, shape, and surface structure of materials at high resolution is scanning electron microscopy (SEM). It functions by directing an electron beam onto the sample, which interacts with the material's atoms to produce a variety of signals, including X-rays, secondary electrons, and backscattered electrons. Detailed images are then produced by detecting and processing these signals. Because of its resolution which can reach nanometers with FESEM (Field Emission SEM). SEM offers substantial advantages over conventional light microscopy, enabling the comprehensive viewing of surface characteristics, topography, and microstructures. The chemical composition of the sample can also be ascertained by elemental analysis when SEM is combined with Energy Dispersive X-ray Spectroscopy (EDS). Because of this, SEM is a vital tool in many disciplines, such as electronics, biology, materials science, forensics, and nanotechnology. Grain boundaries, flaws, fractures, cell surfaces, and even tiny nanoparticles can all be studied with it. SEM has become indispensable in both industrial and scientific applications due to its capacity to study materials at various scales and produce images that resemble three dimensions. Notwithstanding its many benefits, SEM necessitates meticulous sample preparation, particularly for non-conductive materials that can require a thin conductive layer to guarantee precise imaging. [25-27]

Applications: SEM is extensively used to analyze the surface morphology of catalysts, particularly to assess the effects of preparation procedures on catalyst structure.

2.3.3 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is a high-resolution imaging technique that provides detailed information about the internal structure of materials at the atomic scale. Unlike Scanning Electron Microscopy (SEM), where the electron beam scans the surface, in TEM, a beam of electrons passes through a thin sample (usually less than 100 nm thick), and the transmitted electrons are used to form an image. TEM allows for imaging at extremely high resolutions, often at the atomic level, and can provide information about the internal structure, crystallography, and elemental composition of materials. The technique involves a high-energy electron beam passing through the sample, where the electrons interact with the material, and the transmitted electrons are collected by detectors to create an image. TEM is appropriate for observing the atomic arrangement in materials because of its sub-nanometer resolution. Energy Dispersive X-ray Spectroscopy (EDS) and TEM can also be used together to examine the sample's elemental makeup. [28-32]

In SEM, the sample's surface is scanned by an electron beam, and the signals that are released create an image of the surface that provides details about its morphology and topography. While SEM is mostly used for surface imaging, TEM also offers more in-depth information regarding crystallography, flaws, and the arrangement of atoms in materials.

When examining catalysts, TEM is very helpful since it may reveal information about the size, shape, and morphology of catalyst nanoparticles. It may identify crystal flaws or faults, display the lattice structure and crystallinity of the catalyst material. The atomic arrangement and distance between crystal planes can be observed using high-resolution TEM (HRTEM), and crystallographic information can be obtained using selected-area electron diffraction (SAED). Additionally, active sites and surface characteristics that are essential to catalytic activity, such flaws, edges, or steps, can be found using TEM. Furthermore, TEM may investigate the interactions between the support material (like silica or alumina) and the active catalyst phase (like metal nanoparticles), yielding important insights into the stability and dispersion of the catalyst. Elemental analysis is made possible by combining EDS and TEM, which reveals the catalyst composition and verifies the existence of impurities or metal loading. By tracking the changes in catalyst particles over time, TEM also makes it possible to study how nanostructures evolve during synthesis or catalytic reactions. This can reveal information about the stability and performance of the catalyst particles. As a result, TEM is a crucial tool for comprehending the relationships between structure and properties in catalysts, which helps to create more robust and effective catalytic materials.

Applications: TEM is frequently used to assess the homogeneity of catalyst structures and investigate how metal nanoparticles disperse on supports.

2.3.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray by measuring the binding energies of photoelectrons released from atoms upon exposure to X-ray radiation, photoelectron spectroscopy (XPS), a surface-sensitive analytical method, can be used to investigate the elemental composition, chemical state, and electronic state of materials. A monochromatic X-ray beam is directed onto the sample during the XPS procedure, which causes electrons from atoms inner shells to be ejected. These expelled photoelectrons are then detected, and their binding energies are evaluated, revealing information on the elements present and their chemical surroundings. The binding energies of particular elements are represented by the peaks in the XPS spectrum, which can be used to identify the oxidation states and coordination environments of those elements. The binding energies of particular elements are represented by the peaks in the XPS spectrum, which can be used to identify the oxidation states and coordination environments of those elements. Because XPS may offer both qualitative and quantitative elemental composition and is sensitive to the top 1–10 nm of the material's surface, it is very helpful for surface investigation. Additionally, it can be used in conjunction with depth profiling methods such as ion sputtering to examine composition at various material depths. [33-35]

XPS is essential for examining the surface characteristics of catalysts in catalysis. It can identify the oxidation states and elemental makeup of metal components on the catalyst surface, which have a direct impact on the catalyst selectivity and catalytic activity. For example, XPS can determine the various oxidation states of metals such as copper or platinum, giving information about the species that cause catalytic reactions. Furthermore, XPS aids in the investigation of metal-support material interactions, such as metal-oxide bonding, which may have an impact on catalyst performance. By monitoring alterations in the chemical state and surface structure, such as metal sintering or surface contamination, which lead to catalyst deactivation, the approach is also useful for comprehending how the catalyst changes during reaction cycles. Additionally, by identifying adsorbed species on the catalyst surface, XPS can provide information about the behavior of the catalyst in different reaction settings as well as reaction processes. All things considered, XPS is a crucial tool for catalyst development since it helps scientists monitor stability, enhance catalyst design, and boost catalytic efficiency.

Applications: Metal-support interactions, oxidation states, and surface chemistry in catalysts are all frequently studied using XPS.

2.3.5 Brunauer-Emmett-Teller (BET) Surface Area Analysis

One popular way for describing the surface area of materials, especially porous solids, is the Brunauer-Emmett-Teller (BET) method. It is founded on the idea of gas adsorption, which involves introducing a gas usually nitrogen to a substance at liquid nitrogen temperatures, which are approximately -196°C. The gas creates layers on the material's surface as it adsorbs onto it. An adsorption isotherm is produced by plotting the data of the amount of gas adsorbed at various pressures. The BET equation is used to determine the material's surface area using these data. Materials such as catalysts, activated carbons, and nanomaterials benefit greatly from the procedure since it sheds light on their surface characteristics, such as total surface area, pore volume, and pore diameter. [36-38]

$$\frac{P/P_o}{V(1-\frac{P}{P_o})} = \frac{1}{V_m c} + \frac{c-1}{V_m c}\left(\frac{P}{P_o}\right) \tag{2.2}$$

V_m = Estimated number of moles that are monolayer-adsorbed on 1 gm of adsorbent,

P = gas pressure,

P_o = saturated vapour pressure of gas

c = constant

By analyzing the data using this equation, it is able to calculate the surface area of the material, which is significant for applications like catalysis and material design.

Applications: For reactions such as hydrogenation, oxidation, and environmental catalysis, BET analysis is commonly used to evaluate the surface area and porosity of catalysts.

2.3.6 FTIR Spectroscopy

A strong analytical method for learning about a material molecular makeup, functional groups, and structural characteristics based on how it interacts with infrared (IR) light is Fourier Transform Infrared (FTIR) spectroscopy. It is extensively used to examine the chemical structure and functional groups of both organic and inorganic substances in a variety of disciplines, including chemistry, material science, biology, and environmental science. FTIR is very helpful for researching chemical interactions, detecting unknown materials, and verifying the identity of recognized substances.

When a sample is subjected to infrared light in FTIR spectroscopy, it absorbs energy at distinctive frequencies that match the vibrational modes of the material chemical interactions. Certain bonds or functional groups in the chemical can be identified by using the resulting absorption spectrum, which serves as a "fingerprint" of the sample. Based on the idea that molecules absorb infrared light at particular frequencies that match the vibrational frequencies of their internal chemical bonds, FTIR spectroscopy was developed.

The bonds between the atoms in the molecule might stretch, bend, twist, and undergo other deformations as a result of these vibrations. [39-42]

- **Infrared Radiation:** The infrared region of the electromagnetic spectrum lies between the visible and microwave regions. It is typically divided into three regions:
  - **Near-Infrared (NIR):** 12,800–4,000 cm^{-1} (most commonly used in quantitative analysis).
  - **Mid-Infrared (MIR):** 4,000–400 cm^{-1} (most commonly used in FTIR).
  - **Far-Infrared (FIR):** 400–10 cm^{-1} (used for studying heavier atoms and molecular lattices).

The bonds that hold molecules together vibrate at specific frequencies when a sample is exposed to infrared radiation. The link in the molecule absorbs the energy and goes through a vibrational transition if the infrared light frequency coincides with its vibrational frequency.

2.4. Experimental Framework

In this study, different Ni based catalysts are prepared on both alumina and ceria supports. Monometallic, bimetallic and trimetallic catalysts are synthesized and tested in packed bed reactor of internal diameter 11.74mm. Effect of temperature, total metal loading, metal compositions, W/F value, S/M ratio, GHSV value, and other factors are optimized for steam methane reforming. Catalyst with best activity in terms of getting maximum conversion at low temperature with minimum CO selectivity is used in scale up studies. Scale up experiments are carried out in membrane reformer of internal diameter 6.35cm. A comparative analysis is done for small scale data and scale up data for same residence time in both the reactors by maintaining inert gas flow.

2.4.1 Catalyst Preparation

All monometallic, bimetallic and trimetallic catalysts are prepared by using wet impregnation method. Alumina and ceria are used as supports in this study. First of all, gamma alumina in powder form as a support is calcined in a muffle furnace at 970°C temperatures at a rate of 1°C/minute for 6 hours time to obtain the powder of theta alumina as catalyst support. Nickel nitrate hexahydrate is used as a precursor salt for nickel based monometallic catalysts whereas, Iron nitrate nonahydrate, Lanthanum nitrate hexahydrate and cobalt nitrate hexahydrate are used as precursors for iron, lanthanum and cobalt metal loading respectively for bimetallic and trimetallic catalysts preparation. All precursors are added into alumina solution with vigorous stirring at temperature 70°C. This solution is kept for at least 3 hours of time under vigorous stirring in a trimetallic mixture solution. The pH is maintained between 6-8 to obtain a slurry, and then this obtained slurry is kept for drying at 120°C temperature for overnight. This is followed by crushing and calcination at 970°C temperature for 6 hours in a muffle furnace to obtain a trimetallic catalyst. Then this calcinated catalyst is palletized and crushed in a mortar pestle to get the desired size of 180-300 microns for small scale experiments done in reactor of I.D 11.74 mm. Trimetallic Catalyst of best activity is used in larger reactor of I.D 63.5mm in the size range of 3-5mm. All the monometallic, bimetallic and trimetallic catalysts synthesized in current work are listed in Table 2.1, 2.2 and 2.3 respectively. The flow chart of catalyst preparation is shown in Fig 2.1. In chapter 3, Nickel-based catalyst is widely used for SMR due to its low cost and high catalytic activity. CeO_2 is a favored support as it mobilizes the lattice oxygen and reduces the coke formation and CO selectivity. In the current work, monometallic catalysts were prepared on both alumina and ceria supports. Ɵ-alumina is used for the catalyst preparation. γ-Alumina is converted into Ɵ-alumina by calcining it at high temperature with heating rate 1°C/min. Various metals such as Ni, La, Fe and Co are used to prepare monometallic catalysts on both alumina and ceria supports. The complete characterization of the catalysts was performed. The results showed Ni/Al_2O_3 and Ni/CeO_2 catalysts are the most suitable catalysts towards steam methane reforming with high catalytic activity. The effect of support shape and calcination temperature on SMR activity is also found at different operating temperatures. Ni/CeO_2 of different shapes (nanocube and nanorod) are also synthesized. For each condition conversion, CO, and CO_2 selectivity are calculated. The results show the CeO_2 morphology has a considerable effect on conversion, CO selectivity but commercial ceria showed high conversion with low CO selectivity as compared to shapes. After comparative study of different morphologies of ceria, Ni based monometallic catalyst synthesized on commercial ceria support showed good catalytic activity.

Table 2.1 Monometallic Catalysts synthesized on alumina and ceria supports

Monometallic Catalysts	Support (wt%)	Total Metal loading (wt.%)
Ni/Al_2O_3	90	10
Co/ Al_2O_3	90	10
La/ Al_2O_3	90	10
Fe/ Al_2O_3	90	10
Ni/CeO_2	90	10
Co/ CeO_2	90	10
La/ CeO_2	90	10
Fe/ CeO_2	90	10

Table 2.2 Bimetallic Catalysts synthesized on alumina and ceria supports

Bimetallic Catalysts	Total Metal loading (wt%)	Ni (wt%)	La (wt%)	Fe (wt%)	Co (wt%)
Ni-La/ Al_2O_3	10	7.5	2.5	-	-
Ni-Fe/ Al_2O_3	10	7.5	-	2.5	-
Ni-Co/ Al_2O_3	10	7.5	-	-	2.5
Ni-La/ CeO_2	10	7.5	2.5	-	-
Ni-Fe/ CeO_2	10	7.5	-	2.5	-
Ni-Co/ CeO_2	10	7.5	-	-	2.5

Table 2.3 Trimetallic Catalysts synthesized on alumina support

Trimetallic Catalysts	Total metal loading	Nickel	Iron	Lanthanum	Cobalt
Ni-Fe-La/ Al_2O_3	10	7.5	2.0	0.5	-
Ni-Co-La/ Al_2O_3	10	7.5	-	0.5	2.0
Ni-Co-Fe/ Al_2O_3	10	7.5	0.5	-	2.0

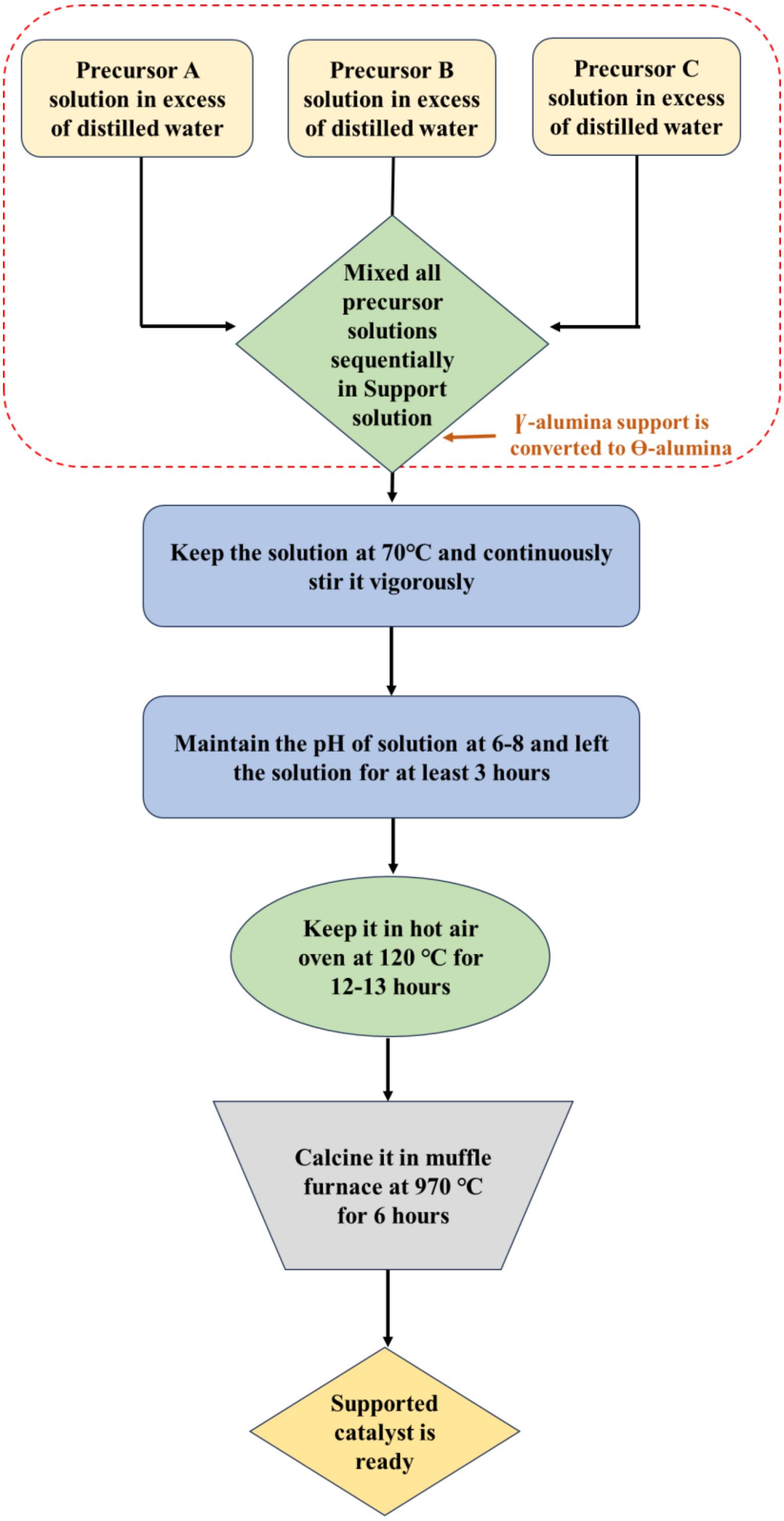

Fig. 2.1 Flow chart for synthesis of catalysts

2.4.2 Catalyst evaluation

Steam methane reforming tests were performed at atmospheric pressure in a packed bed reactor where the catalyst is filled at the middle section of the reactor where temperature is precisely controlled. The Inconel reactor with an internal diameter of 11.74mm was thermally insulated to avoid any heat loss to the reactor. The temperature of catalyst bed was monitored using K-type thermocouple mounted on the top of the catalyst bed. The schematic diagram of catalytic reformer is shown in Fig 2.2. The Catalyst (180-300 microns) weighed 0.76gm mixed with quartz in 1:1 ratio was placed at the middle section of the reactor. Similarly, trimetallic catalyst (3-5mm) with maximum conversion at low temperature with minimum CO selectivity is tested in scale up reactor which is shown in Fig 2.3. Initially, the catalyst was reduced in the presence of 10 vol% H_2 in nitrogen gas environment for 2 hours at 900 °C.The temperature of the reaction was varied from 500-800°C. Water was fed to the packed bed reactor using high pressure metering pump (Eldex optos pump, USA) and gases flow were maintained through mass flow controllers (Bronkhorst).

The mixture of CH_4, N_2 and steam was preheated up to the reaction temperature. The outlet of the reactor was connected to the condenser to condensate excess of water and then condensate was collected and separated using gas liquid separator. The reactor effluent consists of H_2, CO, CO_2, unreacted CH_4 were analyzed using gas chromatography (Nucon GC 1105 trace). The gases were analyzed using a thermal conductivity detector (TCD) using Porapaq Q (I.D 2mm, length 1m) and Molecular sieve column (I.D 2mm, length 3m) arranged in parallel. The conversion (Eqs. 3), CO selectivity (Eqs. 4), CO_2 selectivity (Eqs. 5) and H_2 Yield (Eqs. 6) was calculated by using GC data and measured flowrates. Where, f is molar flow rate of components.

$$\%X_{CH_4} = \left(\frac{f_{CO,out}+f_{CO_2,out}}{f_{CH_4,out}+f_{CO,out}+f_{CO_2,out}}\right) * 100 \tag{2.3}$$

$$\%S_{CO_2} = \frac{f_{CO_2,out}}{f_{CO,out}+f_{CO_2,out}} * 100 \tag{2.4}$$

$$\%S_{CO_2} = \frac{f_{CO,out}}{f_{CO,out}+f_{CO_2,out}} * 100 \tag{2.5}$$

$$Y_{H_2} = \frac{(f_{H_2})out}{(f_{CH_4})in} \tag{2.6}$$

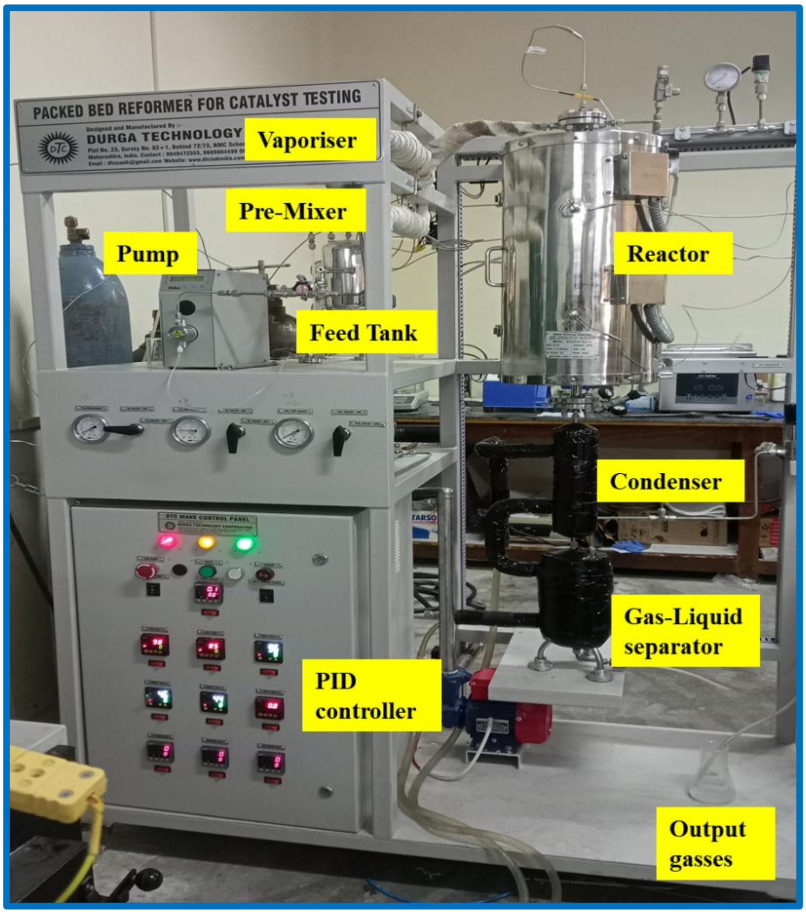

Fig. 2.2 Schematic diagram of packed bed reactor of internal diameter 11.74mm

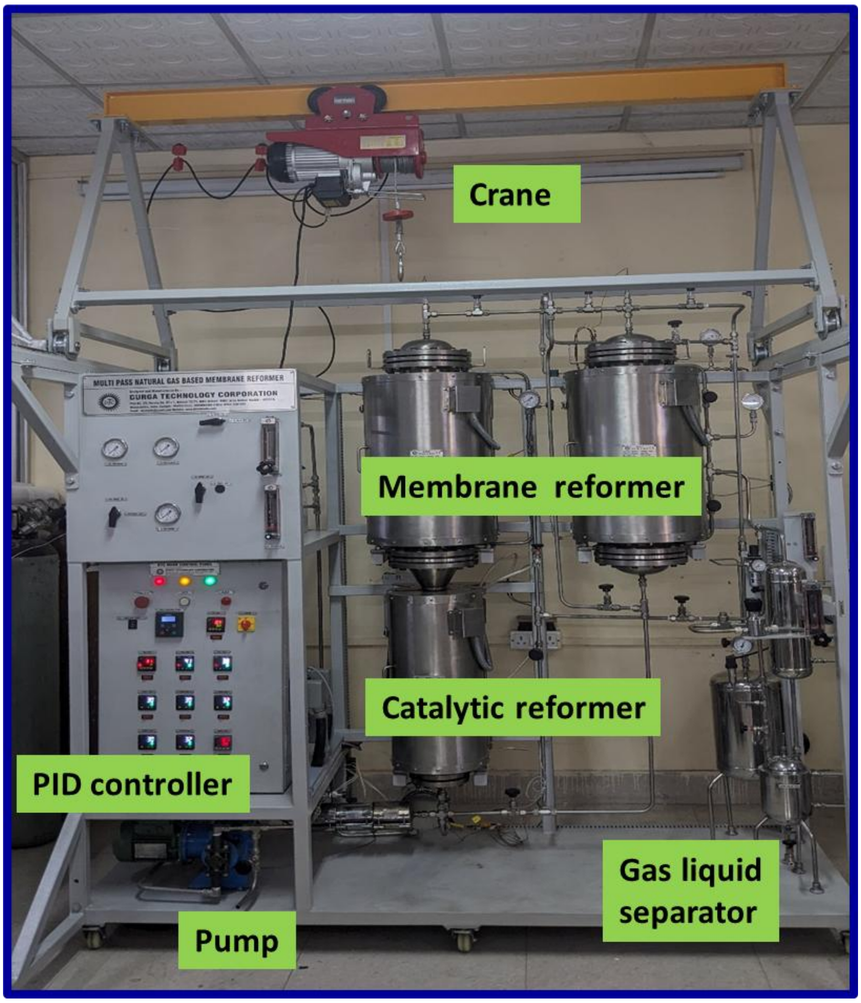

Fig. 2.3 Scale up reactor of internal diameter 6.35cm

2.4.3 Gas Chromatography (GC)

Gas chromatography (GC) is a popular analytical technique for the separation and analysis of gaseous or volatile substances. It works by partitioning a sample between a mobile phase, which is an inert carrier gas like helium, nitrogen, argon, and a stationary phase coated in a column. The sample is introduced by an injection mechanism, with gaseous samples injected directly and into the column. Separation happens when different components of the mixture interact differently with the stationary phase, resulting in unique retention durations. The separation process is heavily reliant on the column, which might be packed or capillary. The type of stationary phase used is determined by whether the analytes are polar or non-polar. When the separated components exit the column, they are identified using a variety of detectors, including a Thermal Conductivity Detector (TCD) for permanent gases, a Flame Ionization Detector (FID) for hydrocarbons, and Mass Spectrometry (MS) for precise chemical identification. The detector response produces a chromatogram, with each peak representing a specific gas, and the area under the peak proportional to its concentration.

Gas chromatography (GC) is widely utilized for gas analysis in several applications, including determining syngas composition (H_2, CO, CO_2, CH_4), natural gas analysis, monitoring pollutant emissions, and evaluating catalyst performance. The technology is extremely sensitive, efficient, and capable of resolving complicated gas combinations, making it an invaluable tool in environmental, petrochemical, and industrial research. Its short analysis time, excellent resolution, and flexibility to many types of gases make it the best approach for precise and accurate gas quantification.

Table 2.4 Calibration factors used in analysis of GC results for mixture of gases

Peak ID	**Retention Time (min)**	**Peak Width (min)**	**Factor**
CO_2	1.138	0.100	1.207E-004
H_2	2.008	0.430	1.223E-005
N_2	4.008	0.190	1.174E-004
CH_4	6.598	0.440	3.496E-005
CO	7.738	0.300	1.105E-004

In this study, mixture of gases is analyzed for steam methane reforming using thermal conductivity detector. Argon gas is used as inert carrier gas for which thermal conductivity difference is compared. A calibration mixture is used for analyzing the gases for which all the factors such as retention time for particular gases and calibration factors for which mixture is prepared are mentioned in Table 2.4.

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