

CHAPTER 3  
EXPERIMENTAL

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**3. 1. Catalyst preparation :-**

Catalysts were prepared by incipient wetness impregnation techniques. Aqueous solutions of the following precursor salts using ruthenium(III)chloride hydrate (  $\text{RuCl}_3 \cdot x \text{H}_2\text{O}$  ,  $x = 3$  , Merk chemie ) , rhodium chloride hydrate (  $\text{Rh Cl}_3 \cdot x \text{H}_2\text{O}$  ,  $x = 2$  , Alfa Aesar ) , and iridium (III) chloride hydrate (  $\text{IrCl}_3 \cdot x \text{H}_2\text{O}$  ,  $x = 3$  Merk chemie ) as the precursor compound .Weighed amounts of every salt were dissolved in distilled water at  $25^\circ\text{C}$  , while 4gm of the carrier  $\gamma$ -alumina ( Puralox , Condea ) were added to the solution under continuous stirring at  $25^\circ\text{C}$  .

The resulting suspensions were then dried in an oven at  $110^\circ\text{C}$  for 24 h , and the resulting powder particles were calcined in air at 773K for 4h .The loading of the metal was fixed at 0.5 wt % .

Before use , the samples were reduced in situ in pure hydrogen (  $20\text{cm}^3 \text{min}^{-1}$  ) for 6 h at 823K .The calcined catalysts are denoted M (O) /  $\gamma\text{-Al}_2\text{O}_3$ . The catalysts reduced in  $\text{H}_2$  are denoted M /  $\gamma\text{-Al}_2\text{O}_3$  .

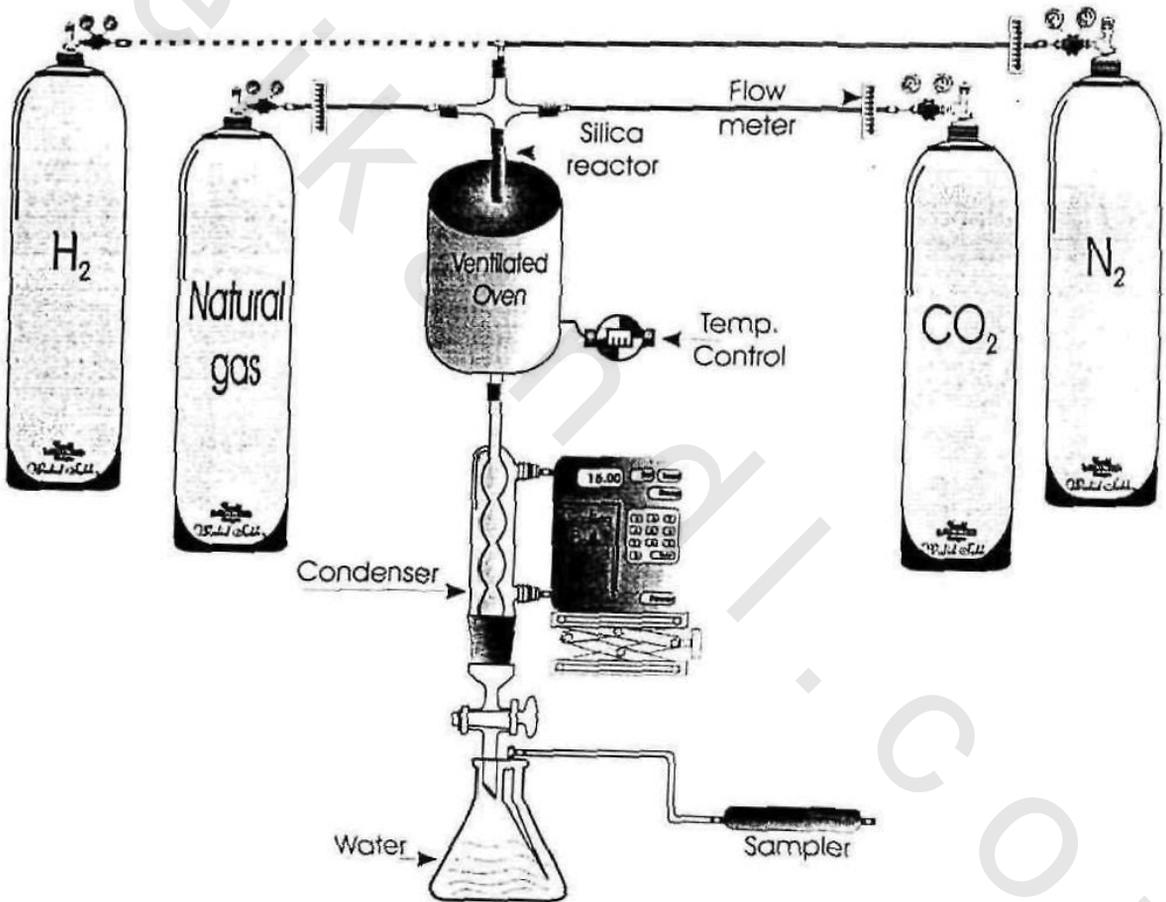
Finally, we have three catalysts 0.5 wt % Rh /  $\gamma\text{Al}_2\text{O}_3$  , 0.5 wt % Ru /  $\gamma\text{-Al}_2\text{O}_3$  , and 0.5 wt % Ir /  $\gamma\text{-Al}_2\text{O}_3$  .

**3. 2. Experimental Setup Fig. ( 3.1 ) :-**

All the catalysts were tested under atmospheric pressure in a fixed - bed vertical silica reactor ( i.d. .13mm , 80 cm in length ) , the reactor was packed with 2gm catalyst and porcelain beads having more or less size of the catalyst particles (  $200 \mu$  ) between two layers of ceramic fibers . The reactor was placed in a ventilated oven ( the catalyst bed height was between 10 and 12 cm ) , the temperature was controlled by means of

a K - type thermocouple , placed in a thermowell in the middle of the catalyst bed . A reaction mixture of N.G : CO<sub>2</sub> : N<sub>2</sub> in proportions 1:1:4 regulated by mass flow controllers was introduced to the sample by switching a four- way valve located at the reactor inlet .

An ice - cold trap was set between the reactor exit and gas sampling to remove the water formed during reaction .The experimental setup is as shown in Fig (3.1) .



**Fig. (2.1). Experimental setup**

### **3. 3. Reaction Conditions :-**

The reaction of N.G with CO<sub>2</sub> was tested over Ru /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Rh /  $\gamma$ Al<sub>2</sub>O<sub>3</sub>, and Ir /  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> at three reaction temperatures namely ; 873°K , 973°K and 1073°K , and four space velocities ,18000 ccg<sup>-1</sup>h<sup>-1</sup> , 36000 ccg<sup>-1</sup>h<sup>-1</sup> , 45000 ccg<sup>-1</sup>h<sup>-1</sup>, and 60000 ccg<sup>-1</sup>h<sup>-1</sup> . These space velocities were achieved by adjusting the mass flow controllers to give flow rates of 600 ccmin<sup>-1</sup>, 1200 ccmin<sup>-1</sup>, 1500ccmin<sup>-1</sup> , and 2000 ccmin<sup>-1</sup> respectively.

### **3. 4 . Procedure of N.G Reforming Reaction Runs :-**

The catalyst bed was first flushed with nitrogen at the calculated flow rate , then CO<sub>2</sub> gas was introduced with the calculated flow rate . Finally , N.G gas was introduced with the calculated flow rate , where the sum. of three flow rates give the total flow rate corresponding to a certain space velocity tested in the ratio 1:1:4 for N.G , CO<sub>2</sub> and N<sub>2</sub> respectively . With the heater turned on and the catalyst bed temperature adjusted at the desired set point, the catalyst bed was left for at least 15 min to be sure that the steady state conditions were achieved . Use a gas sampling for at least 60 min to receive the gas mixture , this sample is called control sample .

Adjust the temperature control at 873K , the catalyst bed was left for at least 15 min to be sure that the temperature was almost constant, then collect the gas mixture at 873K for at least 60 min , these steps were repeated at 973K , and 1073 K .

Finally, switch of N.G , CO<sub>2</sub> flow and cool the catalyst bed to room temperature with nitrogen flow. After each run the tested catalyst was reduced in situ with pure hydrogen at 20 cm<sup>3</sup>min<sup>-1</sup>for 2h at 823K .

### **3.5 . Analysis of Gas Mixture :-**

The components of natural gas  $C_1$ ,  $CO_2$ ,  $C_2$ ,  $C_3$ ,  $i-C_4$ ,  $n-C_4$ ,  $i-C_5$ ,  $n-C_5$ ,  $C_6$ , and  $C_7$  and the produced synthesis gases (  $H_2$  and  $CO$  ) were analyzed using Agilent 6890 plus HP gas chromatograph, equipped with thermal conductivity detector (TCD) and flame ionization detector (FID) , using three different columns , fused silica plot Q capillary column 15 meter in length and 0.35 mm internal diameter , attached to the TCD , the packed column DC 200 of stainless steel in type , 10 feet in length and 1/ 8 inch in diameter , attached to the FID and fused silica molecular sieve capillary column of 15 meter and 0.25 mm internal diameter , attached to the TCD .

The elution of the studied gas mixtures was achieved with temperature programming from 60 to 200°C at a rate 10° C min<sup>-1</sup> .

Nitrogen ( oxygen - free ) was used as a carrier gas for complete analysis of natural gas , while helium was used as carrier gas in the case of detection of  $CO$  and  $H_2$  .

Flow rates were measured from the end of the column with a soap bubble flowmeter . Methane as an unreturned marker was used to correct the dead volume in the column in the case of FID , and air used as a marker in the case of TCD .

The quantitative analysis of the liberated gas mixture was achieved using standard natural gas sample of known composition according to the standard ASTM method ( D 1945 – 96 (1996) ) . The injector and detector temperatures are 200 and 250°C respectively .

The area under the resolved chromatographic profile was estimated by integration using the connected Epson data station unit .