CHAPTER 4

PREPARATION OF METHANOL SYNTHESIS CATALYST

Catalysts used for methanol synthesis can be devided as following.

1. Catalysts containing only one metal oxide eg. ZnO, CuO, Cr_2O_3.
2. Mixed catalysts
   - Binary catalyst containing two metal oxides eg. ZnO/CuO, ZnO/Cr_2O_3, Cu/ThO_2.
   - Ternary and Quaternary catalysts containing three and four metal oxides respectively eg. $Cu/ZnO/Al_2O_3$, $Cu/ZnO/Cr_2O_3$, $Cu/ZnAl_2O_4/ZnO$ and the combination of Cu-Co-transition oxide-alkali oxide etc.

Ternary compositions $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Cr_2O_3$ are currently the most important industrial catalysts. In this study, a $Cu/ZnO/Cr_2O_3$ catalyst with atomic ratios of Cu:Zn:Cr = 31:38:10 was prepared for methanol synthesis. It was prepared from copper nitrate, zinc oxide and chromium oxide. The procedure was as follows:

1. Dissolves 5.9272 gm copper nitrate ($Cu(NO_3)_2.3H_2O$) completely in 50 ml distilled water. Precipitate the copper nitrate by adding quickly 3.7 ml of ammonium water from a pipette and mixing the solution for (at least) 2 minutes.

2. Take out the mixture and centrifuge for 10 minutes to separate the precipitate. Then measure and record the pH of the top solution (the pH meter was calibrated with 6.86 and 9.18 buffer solutions)

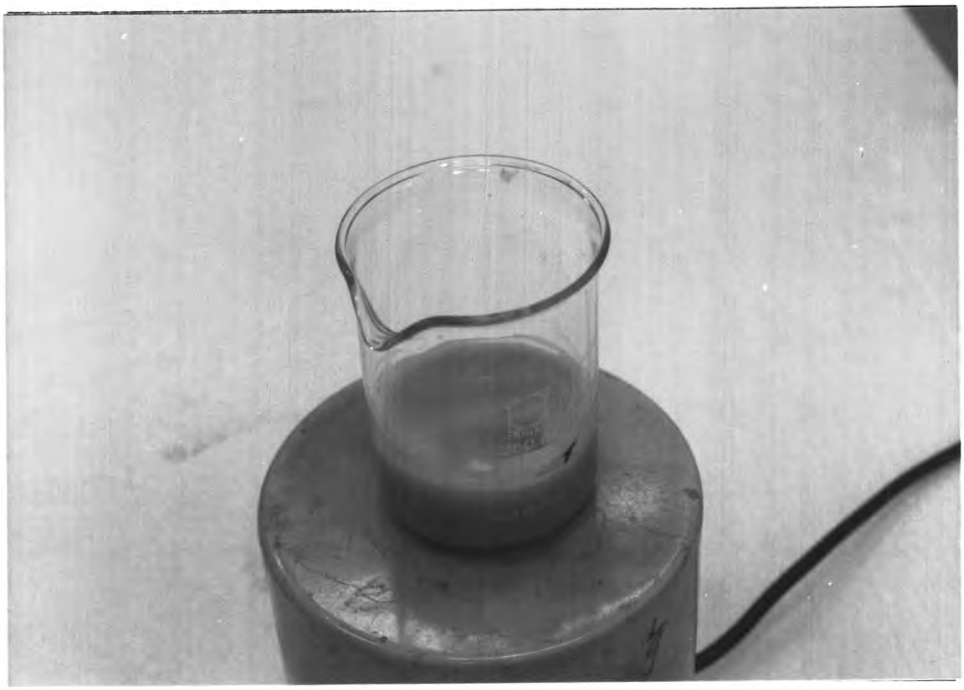
3. Decant the liquid, wash the precipitate with distilled water 50 ml and centrifuge out the precipitate for 10 minutes. After each washing, measure and record the pH of the top solution. Repeat the washing procedure four more times.

4. Take the precipitate out and grind thoroughly in a motar for 30 minutes.

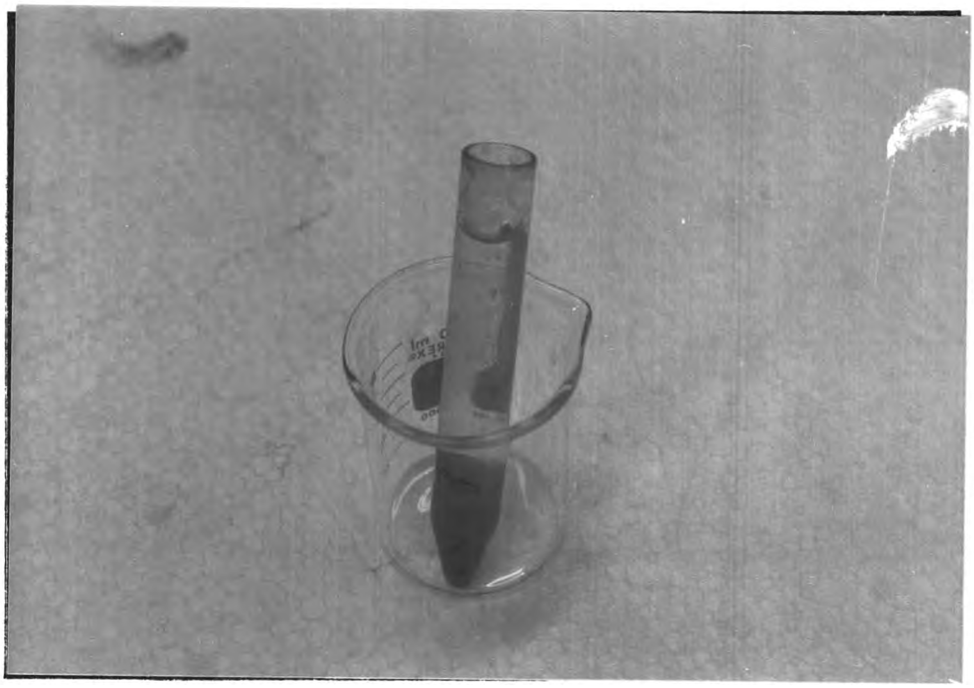
5. Add 0.7835 gm of chromium oxide (CrO_3) powder and mix-grind for 1 hour. (Use hand gloves and handle with precaution).

6. Dry the mixed paste in an oven at 70-80°C for 3 hours.

7. Add 2.4504 gm of zinc oxide (ZnO) powder to the dried paste and mix-grind rigorously for 30 minutes to obtain about 5 gm of $Cu/ZnO/Cr_2O_3$ with the atomic ratios of Cu:Zn:Cr = 31:38:10.



a. Solution of $Cu(NO_3)_2.3H_2O$ + ammonium water



b. The obtained precipitate from reaction

$Cu(NO_3)_2.3H_2O + NH_4OH$

c. Mixed-Grind of the precipitate and CrO_3 from the oven

d. Mixed-Grind of about 5 gm. $CuO/ZnO/Cr_2O_3$ with the atomic ratios of Cu:Zn:Cr = 31:38:10

Figure 4.1 The Obtained Catalyst at Each Step of this Preparation

4.1 Reduction of Methanol Synthesis Catalyst

After preparation, the above catalyst needed to be reduced by a mixed gas ($CO:H_2 = 2:1$) diluted with N_2 in a furnace. (The facility for catalyst reduction including the furnace was set up by ourselves). The purpose of reduction was to enhance and stabilize catalyst activity.

Fig. 4.2 shows a schematic diagram of the catalyst reduction system. Here A,B,C were fine metering valves, E was a stop valve, F and G were pressure gauges. Valves A,B,C and pressure gauges F,G were used to adjust the flow rates of CO, H_2 and then N_2 to obtain the desired gas composition. The bubble flow meter was used to measure volumetric flow rate. Nitrogen gas which passed through line CGE was for purging CO gas from the system. The materials of construction were all Swagelok fittings for safty and high reliability.

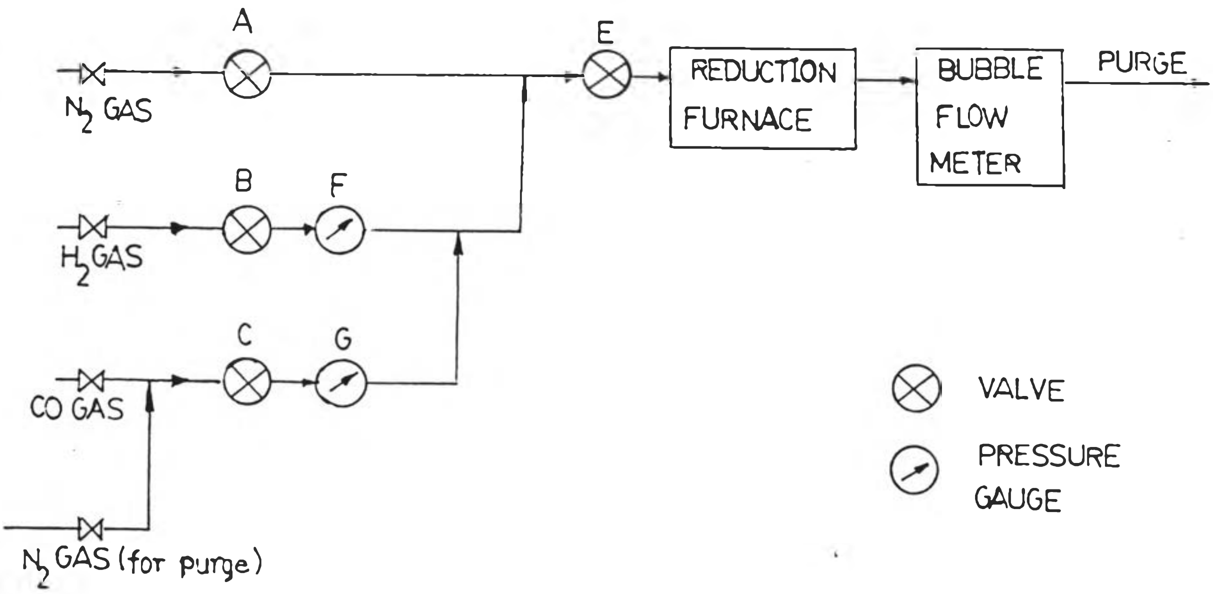


Figure 4.2 Schematic Diagram of the Catalyst Reduction System

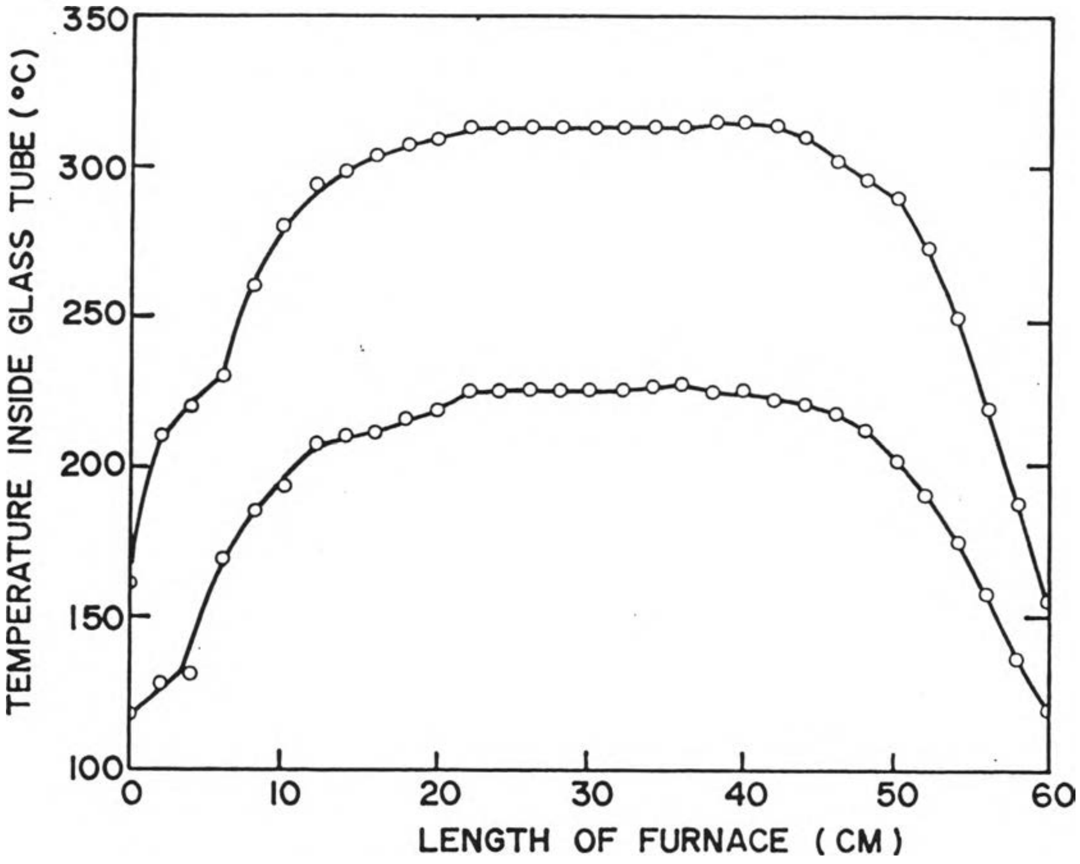


Figure 4.3 Axial Temperature Distribution within the Glass Tube of the Catalyst Reduction Furnace

The heating furnace for catalyst reduction was molded by pouring refractory cement in an aluminium cast, and then 8 electrical heating wired were installed in parallel. A pyrex glass (100cm long, 5cm outer diameter) was placed inside the furnace and the applied electric power to the heating wires was adjusted via a slidac. After the whole furnace had reached the desired steady-state temperature, a CA (chromel-alumel) thermocouple was inserted into the pyrex glass to measure the axial temperature distribution. From the measured temperature distribution, portions of the heating wires were stretched and compressed accordingly (by trial and error) until an axial temperature variation of ± 3 °C was achieved for the middle 20-cm region of the furnace. The check procedure was repeated to ensure uniform axial temperature distribution around 200°C, and 300°C respectively, under no-flow condition. Fig. 4.3 shows the obtained axial temperature profiles of the catalyst reduction furnace at around 200°C and 300°C. Fig 4.4 is a photograph of the inside of the furnace.

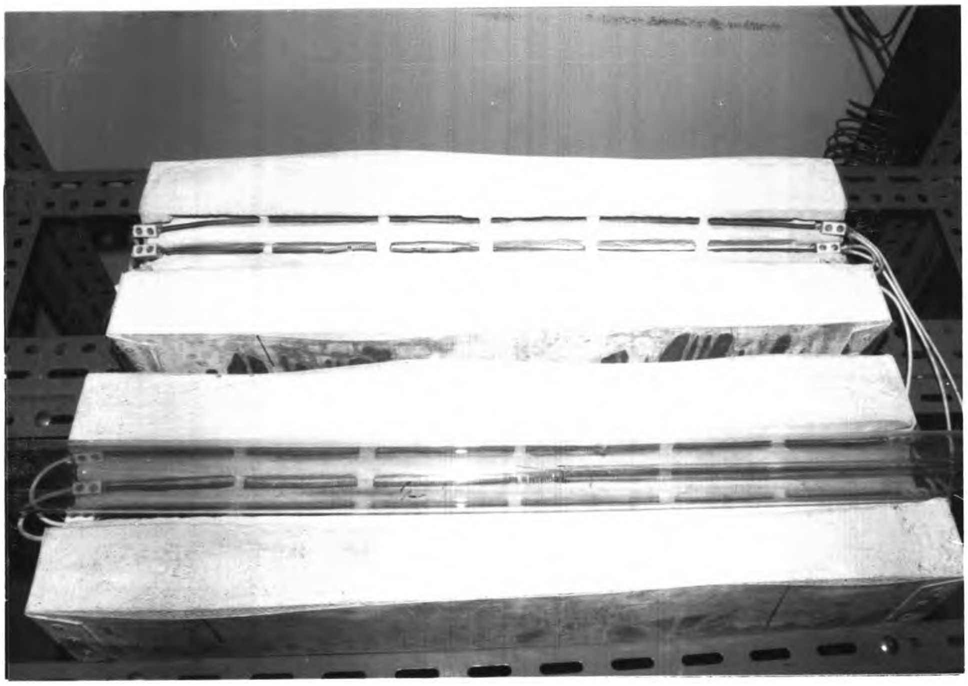


Figure 4.4 The Inside of Catalyst Reduction Furnace

After fabrication, a leak test was carried out on the catalyst reduction set. First nitrogen gas at 1, 4 and 7 atg, respectively,was used. During each test, a soapy solution was squirted onto all areas susceptible to leakage, such as unions , joints, and valve handles. Next helium gas at 10 and 20 atg was used in place of nitrogen gas.

The catalyst to be reduced was spread out on a ceramic boat and placed in a pyrex glass tube within the reduction furnace. The boat was placed at a point where a uniform axial temperature profile had been found a priori.

A desired flow ratio of CO/H_2 = 1/2 was set by 1) opening valve C (CO line) and adjusting the flow rate at the bubble flow meter to the desired valve (50 ml/hr in this case), and 2) opening valve B (H_2 line) and adjusting it until the total flow rate at the flow meter was three times the former (150 ml/hr). To prevent possible reduction in CO flow by newly applied pressure of H_2, the regulated pressure of CO from the tank should be set slightly higher than that of H_2. Finally, flow of dilution gas (N_2) was set by opening and adjusting valve A until a total flow rate of N_2, CO and H_2 at the bubble flow meter was 3600 ml/hr. In this way a flow ratio of $CO:H_2:N_2$ = 1:2:69 was obtained.

After the desired flow conditions had been obtained, the inside temperature above the boat was raised at a rate of 2°C/min from room temperature to 180°C, 0.5°C/min form 180°C to 230°C and held constant until the colour of the entire catalyst turned to black. To ensure complete reduction the temperature was then raised from 230°C to 250°C at a rate of 2°C/min (see fig. 4.5)..

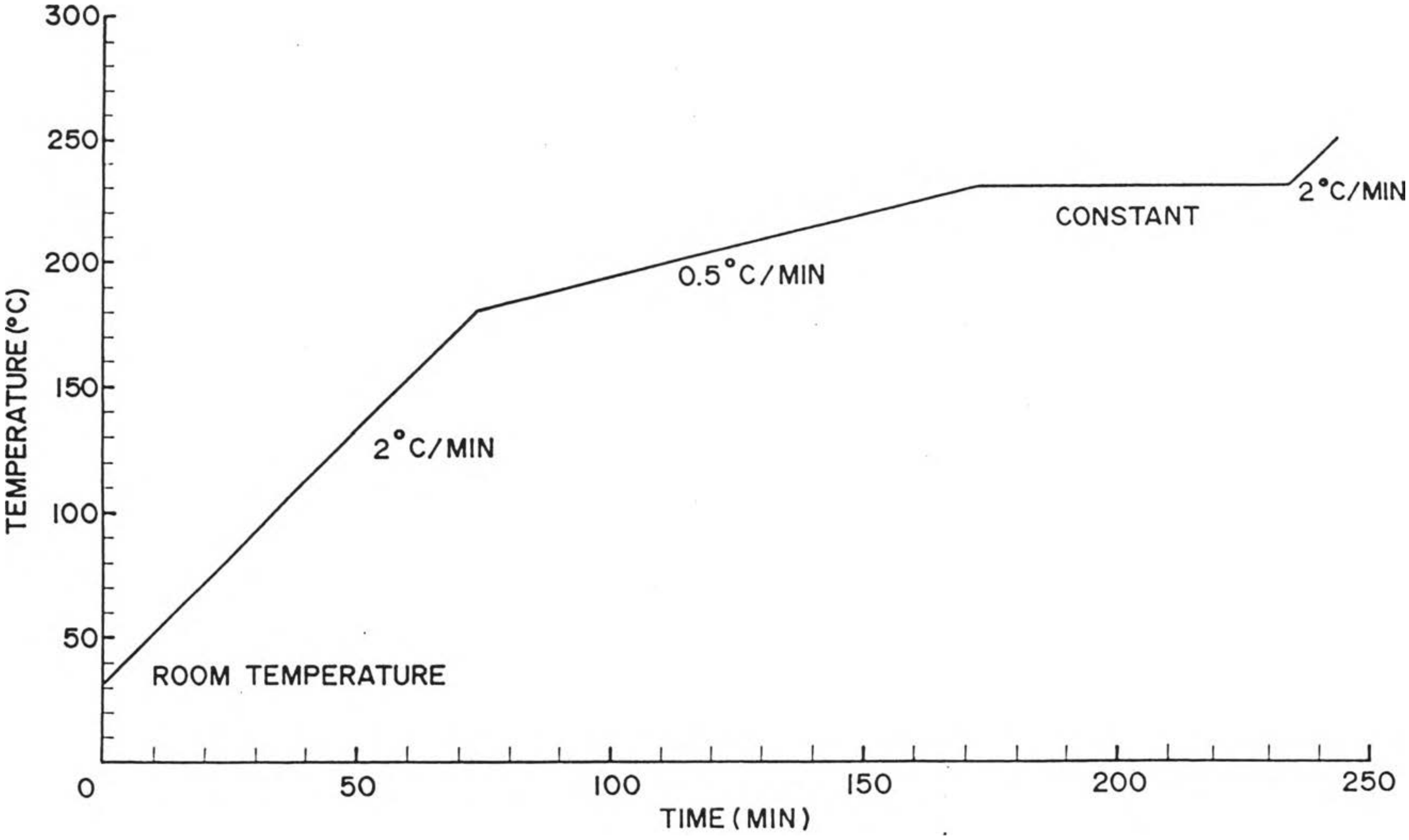


Figure 4.5 The Reduction Temperature of Methanol Synthesis Catalyst

After cooling down, the reduced catalyst powder was kept in an air-tight.

When it was time to carry out experiment, the powder was weighed at 0.24 gm and then compressed to a volume of 0.12 ml to obtain a pellet with 2 gm/ml density. The pellet was next cut up and screened to classify fragments of size between mesh #16 and 30. These classified fragments were ready to pack into the reactor for methanol synthesis.

Besides the above self-prepared catalyst, an industrial catalyst was also studied.

Fig 4.6 The catalyst reduction system

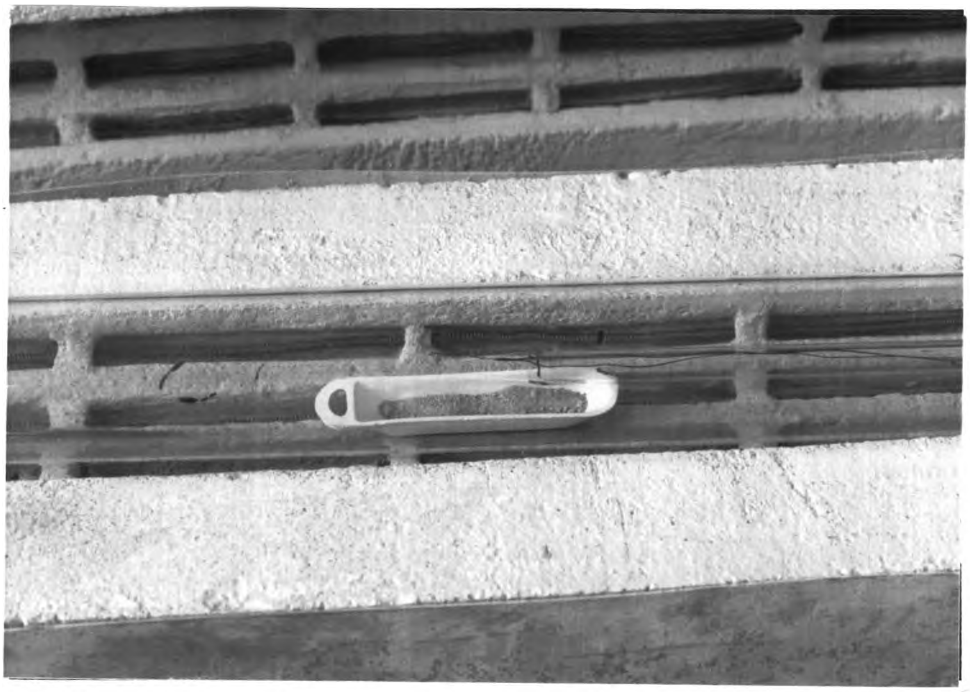


Figure 4.7 Prepared Catalyst on the boat in the Reduction Furnace

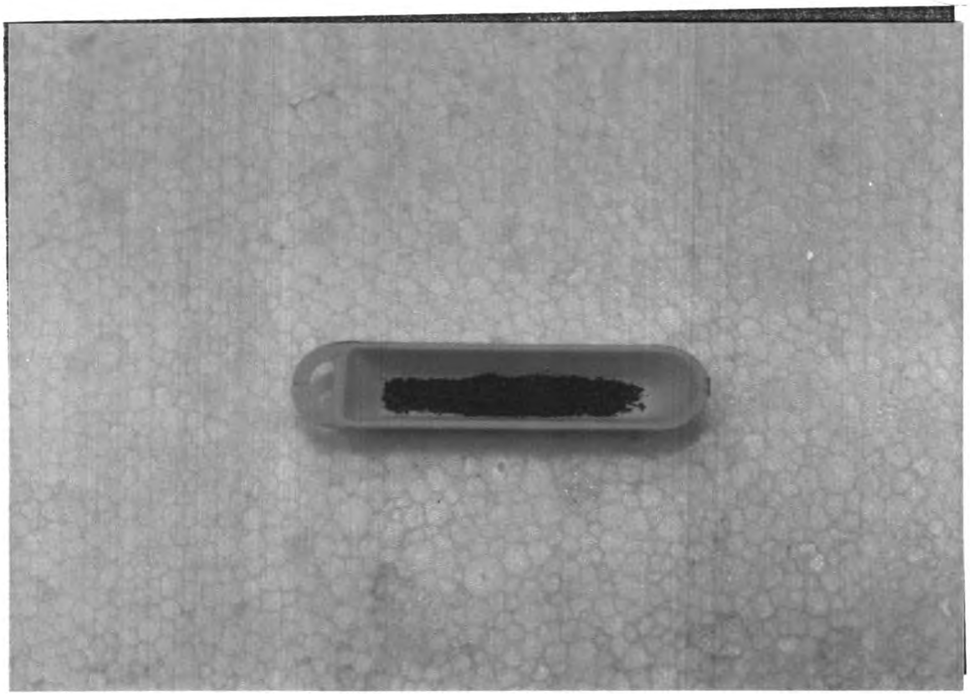


Figure 4.8 The Obtained Reduced Catalyst