COMPARATIVE STUDY OF PREPARED AND INDUSTRIAL LOW TEMPERATURE SHIFT CATALYSTS

A THESIS FOR

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

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CERTIFICATION OF THESIS WORK

We, the undersigned, certify that **Mohammad Abdul Alim Dewan**, a candidate for the degree of **Master of Science in Engineering (Chemical)**, has presented his thesis on the subject **"Comparative Study of Prepared and Industrial Low Temperature Shift Catalysts"** that the thesis is acceptable in form and content, and that the student demonstrated a satisfactory knowledge of the field covered by this thesis in the oral examination held on the February 27, 2005.

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DECLARATION

I do hereby declare that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

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ABSTRACT

Experimental studies have been carried out to investigate the effect of preparation methods, preparation variables and operating conditions on the activity and, especially, on the life of the laboratory scale Low Temperature Shift (LTS) catalysts. In every case, the results observed on industrial catalyst are compared with the results obtained using the prepared catalysts. Copper based catalysts have been prepared following co-precipitation, solution and incipient wet impregnation technique. The activity test results, presented graphically, show that preparation methods have considerable influence on LTS catalyst. To find out the optimum catalyst composition, reduction and reaction conditions, the effect of CuO concentrations (15-41%), ZnO/Al_2O_3 ratio (0.73-4.27), reduction temperature (150-350°C), reduction time (1-6 hr), and reaction temperature (150-400°C) on the activity of the prepared catalysts has been studied. The conversion of carbon monoxide is observed to change about 90% when concentration of CuO in catalyst is increased from 15 to 41%. Significant increase of the rate of reaction has been noticed with increasing ZnO/Al_2O_3 ratio. Industrial catalyst and the catalysts prepared by impregnation method have been used for short-term and long-term stability tests to establish the deactivation trends. The physical properties of the catalysts, which are used to correlate with the results of activity testing, viz. total pore volume, active metal surface area and Temperature Programmed Reduction (TPR) profile have been determined using conventional characterization methods. Considerable influence of preparation method and catalyst composition on BET area, pore volume and TPR profile of the catalysts has been observed.

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NOMENCLATURE

a - Hydrogen in feed gas, mol
b - Carbon monoxide in feed gas, mol
$\boldsymbol{b}$ - Moles of steam per mole of CO
C - Constant
$\mathbf{D}$ - Diffusion coefficient, m^2/sec
$\boldsymbol{D}$ - Dispersion
E_L - Activation energy, J/mole
$\boldsymbol{n}$ - Moles per 100 moles of dry gas
N_o - Avogadro number, 6.023×10^{23}
N_{total} - Total number of metallic atoms
K - Equilibrium constant, mol/lit/sec
K_{AS}, K_{BS} - Constant
K_{LS}, - Standard activity for one year old catalyst, moles /sec/atm (abs)/m^3
K_v - Fugacity correction factor
k_f - Forward rate constant, mol/lit/$(mol)^{0.1}$
P_x - Partial pressure of the reactants, atm
P - Total pressure, atm
P_0 - Saturation vapor pressure of Adsorbate, atm
K_D - Equilibrium constant
r - Reaction rate, mol/wt.cat/time
r_f - Forward rate, mol/wt.cat/time
S_{BET} - Surface area by BET, m^2
T - Temperature, K
T_{room} - Room temperature, K
T_{LS}, T_{AS}
and T_{BS} - Standard temperatures, K
v - Calibrating gas volume, m^3
V - Volume of adsorbed gas, m^3
V_m - Volume of a monolayer of adsorbate, m^3
V_{mol} - Molar volume of the adsorbate, m^3
V_{tp} - Equivalent total pore volume, m^3
X - Minimum steam requirement, mol
y - CO converted, %

INTRODUCTION

1.1 INTRODUCTION

Low temperature shift reaction or Water gas shift (WGS) is the reaction of water and carbon monoxide to produce hydrogen and carbon dioxide and is an important step in the production of H_2 via the steam reforming of hydrocarbons. The first industrial process for the catalytic CO conversion was developed by Bosch and Wild in 1912 and put into operation at the Badische Anilin-& Soda-Fabrik (BASF) plant in Germany a few years later (Begum, 1992). This process is now part of the large majority of existing ammonia plants and of many other plants utilizing hydrogen for synthetic purposes. In recent years, Low Temperature Shift (LTS) reaction has obtained renewed interest because of its potential use in fuel processing for fuel cell power generation and depoisoning of town gas. Due to its commercial and economic importance, extensive researches are being carried out to develop efficient catalysts.

In the earlier practice, two stages of high temperature shift were normally used, with some cooling, and perhaps CO_2 removal between stages to improve conversion in the second stage. A high temperature, around 825°F at the outlet of the first converter, was employed because the catalysts available at that time did not give a fast enough reaction rate at lower temperature. Many plants in the late 1950s were to remove CO_2 between the two conversion stages to drive the reaction nearer to completion, even at high temperature, and made methanation feasible as the method of removing final traces of CO. However, the necessity for two stages of CO_2 removal, and the heat exchange required for getting the gas back up to the temperature required for the second shift reaction step, made this approach some what costly although preferable to copper liquor removal in most cases.

The next development was Low Temperature Shift (LTS) Catalyst, a catalyst capable of giving favorable equilibrium conversion at relatively low temperature of 300 to 350°F as compared with 650 to 1000°F for the high temperature catalyst.

Industrially, LTS reaction is carried out at two temperature regimes; the high temperature shift reactors use a Fe_2O_3-Cr_2O_3 catalyst, which can effectively reduce CO from several percentages to the equilibrium CO value dictated by the operating temperature; further reduction of CO takes place at low temperature over a more active catalyst based on Cu-ZnO. This catalyst is very sensitive to temperature excursions, operating in the narrow temperature window of 200-250°C, requires careful activation (in H_2 gas), and is readily deactivated by exposure to air or by water condensation. Thus, this of type catalyst is unsuitable for use with low-temperature fuel cells, under development for automotive applications (Ruettinger et al., 2003)

Generally, the shift reaction is carried out at either high or low pressure. With the development of the high-pressure reforming process, the subsequent CO conversion step has also been operated at pressures of 400-500 psig. The main limitations of catalysts operating at high temperature and pressure arise from a tendency for side reactions such as

$$\mathbf{CO+3H_2 \rightarrow CH_4+H_2O}$$

$$\mathbf{2CO \rightarrow CO_2+C}$$

which cause elemental carbon formation and deposition in the catalyst pores. This destroys both the catalytic activity and its mechanical strength and thus further reduces the hydrogen content of the effluent gas. Literature review on this topic has revealed that there still remain certain questions unanswered regarding the influence of many of the preparation and operating variables on LTS catalyst.

The commercial catalyst consists of an intimate mixture of copper, zinc and alumina oxide, which seems to be the most active catalyst in this field. The most important properties of the catalyst, such as activity, stability, etc., are likely to be dependent on dispersion of the active component, as well as on interaction with the support medium. In this case, activity may be related to the degree of copper dispersion and linked to metal particle size. The method of preparation may have a significant effect on the dispersion, activity and stability of the metal.

A complication in considering the stability of a catalyst in a catalytic reactor is that the conditions inside the reactor usually vary dramatically from one region of the reactor to other. A successful catalyst must then survive these various conditions. In a fixed bed reactor, the conditions at the inlet generally are very different from that at the outlet. In fact, if one is interested in the rational design or selection of a catalyst based on the underlying chemistry, it is essential to know the nature of the real working catalyst which in some cases bears little resemblance to the catalyst a manufacturer supplies.

In principle, one can quickly screen large numbers of catalysts for activity and selectivity. Evaluation of lifetime is by its very nature time-consuming. Many publications including patents present interesting examples of catalyst activity and selectivity with little or no information on catalyst life. In view of the difficulty of evaluating the lifetime for every catalyst with attractive selectivity and activity, an understanding of catalyst design and selection with regard to catalyst life becomes especially desirable.

Since the mid-1960s, Cu/Zn/Al catalysts have been applied commercially in low temperature shift reaction (LTS). Long time after realization, still, there are some problems associated with LTS catalysts. Extensive researches are going on round the world on the following aspects of LTS catalysts:

- The procedure to activate catalyst *in situ*
- Intolerance to temperature excursions
- Size of the shift reactor
- Life of catalyst

In Bangladesh, industries, especially fertilizer industries, face challenges to select the proper catalyst. They need expertise having technological know-how regarding the selection of catalyst, operation and maintenance of catalytic reactor. This research project is aimed to develop expertise in catalytic shift reaction of ammonia plants. It is anticipated that the results of the proposed research project will help in designing and selection of shift catalyst and enable us in planning better operation of our shift conversion units of ammonia plants so as to maximize catalyst life and product yield thereby improving the economics of the process.

1.2 OBJECTIVES

As mentioned earlier that since mid 1960s, Cu/Zn/Al catalysts are being used as commercial catalytic material for Low Temperature Shift reaction, still, there are some problems related to LTS catalyst preparation, activation and stability remain under question. Therefore, the following research objectives have been selected for this study:

- To prepare LTS catalysts in the laboratory using the existing experimental set-up
- To characterize the prepared catalysts using different techniques
- To compare the properties of the prepared catalysts with those of commercial catalysts used in fertilizer industries of Bangladesh

Chapter 2

LITERATURE REVIEW

In this chapter, some aspects of reaction equilibrium and kinetics of CO shift reaction have been reviewed. Special attention has been given on the study of activity, stability and characterization of conventional Cu-based Low Temperature Shift (LTS) or Water Gas Shift (WGS) catalyst prepared using different methods.

2.1 CO SHIFT REACTION EQUILIBRIA

The reaction $CO+H_2O \rightleftarrows CO_2+H_2$ is moderately exothermic (Q=9.7 Kcal/ mol). This reversible reaction is thermodynamically unfavorable at elevated temperatures. In order to achieve high conversions, the reaction is typically run in multiple adiabatic stages, with lower inlet temperatures in later stages. A low CO content at equilibrium is therefore favored by low temperature. Equilibrium constant, K, of this reaction decreases rapidly with increase in temperature, which can be calculated from the equation 2.1 developed by Bryant (1931).

$$
\begin{aligned}
\mathit{LogK} &= 2059\ T^{-1} - 1.5904\ \mathit{LogT} + 1.817 \times 10^{-3}\ T - 5.65 \times 10^{-7}\ T^{2} \\
&+ 8.24 \times 10^{-11}\ T^{3} + 1.5313
\end{aligned}
\tag{2.1}
$$

Some calculated values for K are tabulated in Table A.1, which shows close agreement with experimental values reported by the many independent investigators. Figure A.3 shows that K decreases rapidly with increase in temperature.

To drive the reaction forward, thermodynamically, excess steam is used. The minimum steam requirement for any given percent conversion of CO at a given temperature and atmospheric pressure may be calculated by following equation 2.2 (Slack, 1974) when K is known.

$$X = \frac{(a+b)(c+by)}{K(1-y)b} + by \tag{2.2}$$

Where,

X=minimum steam requirement, mol

K=equilibrium constant for the water-gas shift reaction;

a= hydrogen in the feed gas, mol

b=carbon monoxide in the feed gas, mol

c=carbon dioxide in the feed gas, mol; and

+

y=the amount of CO converted, %

It is to be noted here that there is a strong relationship between steam requirement and the percent conversion of CO at different temperature. Figure A.2 represents the relation between steam ratio and percent CO conversion for parameters of temperature.

The equilibrium CO mole fraction can be calculated by following equation 2.3 (Slack, 1974).

$$K = \frac{n_{CO_2} . n_{H_2}}{n_{CO} . n_{H_2O}} . K_v = \frac{(n_{CO_2} + \Delta n_{CO})(n_{H_2} + \Delta n_{CO})}{(n_{CO} - \Delta n_{CO})(n_{CO} b - \Delta n_{CO})} \tag{2.3}$$

Where 'b' is the moles of steam per mole of CO and 'n' is the indicated moles per 100 moles of dry gas. The fugacity correction term K_v can be considered equal to unity for the conditions of operation of shift converters.

2.2 KINETICS OF CATALYTIC SHIFT REACTION

To obtain kinetic evidence of low temperature shift reaction that proceeds via a formate-type intermediate on the catalyst surface, Hewijenen and Jong (1978) have studied the shift reaction over a Cu/ZnO catalyst. The results have described with Langmuir-type kinetic equations and indicate that both the forward and reverse CO shift are characterized by a relatively stable intermediate formed from one molecule of each of the reactants, $CO{\bullet}H_2O$ and $CO_2{\bullet}H_2$, respectively. They have shown that the decomposition of this complex is rate determining; in both cases the copper surface coverage by the complex is relatively high and varies little in the temperature range of commercial application of the shift reaction.

A comprehensive paper by Koryabkina et al.(2003) presented a study to determine the kinetic parameters for water–gas shift reaction on Cu-based catalysts measured under fuel reformer conditions for fuel cell applications having feed composition 7% CO, 8.5% CO_2, 22% H_2O, 37% H_2, and 25% Ar at 1 atm total pressure and temperature in the range of 200 °C. The rate per unit of Cu surface area at the stated concentrations was 0.8×10^{-6} mol m^{-2} s^{-1} at 200 °C. The overall reaction rate as a function of the forward rate (r_f) is

$$r = r_f(1-\beta) \tag{2.4}$$

Where,

$$r_f = k_f \frac{[CO]^{0.8}[H_2O]^{0.8}}{[CO_2]^{0.7}[H_2]^{0.8}} \tag{2.5}$$

k_f is the forward rate constant, $\beta=([CO_2][H_2])/(K[CO][H_2O])$ and K is the equilibrium constant for the water–gas shift reaction. This expression indicates a strong inhibition on the forward rate by H_2 and CO_2. In this paper, the effect of addition of ceria on Cu catalyst has also been presented. Addition of Ceria decreased the Cu surface area and did not increase the rate per unit of Cu surface area, suggesting that ceria is not a promoter. The addition of ZnO did not increase the rate per unit of Cu surface area either. It was proposed that the kinetics can be explained based on the "Redox" mechanism with $CO^* + O^* \rightleftarrows CO_2^* + {}^*$ as the rate-determining step. From their study, it can be assumed that Cu is the active component and rate mainly depends on Cu surface area.

There are three main factors, which are important to derive the rate equation: reaction kinetics, diffusion of reactants into and within the catalyst, and diffusion of reactants in the gas stream. This rate equation is based on a wide range of data over the pressure range of 1 to 50 atm on a variety of catalysts. Kinetic rate equations are mainly based on two reaction mechanisms: the catalyst either acts simply as an adsorbent on which the reactants react, or takes part in the reaction as is successively oxidized and reduced by the adsorbed reactants. If the rate-determining step is assumed to be the reaction of CO, with other steps in the reaction mechanism at equilibrium, a kinetic expression can be obtained. Rate of reaction can be express as equation 2.6 (Slack, 1974).

$$Rate = \frac{KP_{CO}}{1 + K_B P_{H_2O} + K_D P_{CO_2} + \frac{K_E K_D}{K_C K_B} \frac{P_{CO_2} P_{H_2}}{P_{H_2O}}} \left(1 - \frac{P_{CO_2} P_{H_2}}{K_P P_{CO} P_{H_2O}}\right) \tag{2.6}$$

Where, P_{CO}, P_{H2O}, P_{H2}, P_{CO2}, etc. are the partial pressure of the reactants.

This equation assumes that there are no diffusional limitations and K_B, K_D, K_C and K_E are equilibrium constants for the various steps and vary from catalyst to catalyst. If the constants K_B through K_E are small, Equation 2.6 can be reduced to

$$Rate = kP[CO]\left(1 - \frac{[CO_2][H_2]}{K_p [CO][H_2O]}\right) \tag{2.7}$$

Where, [CO] etc. are the molar fractions and P is total pressure.

Again, when rate of reaction is controlled by the diffusion of CO into the catalyst pores, the right hand side of Equation 2.7 can be modified to

$$Rate = [kD]^{1/2} P[CO](1-\frac{[CO_2][H_2]}{K_p[CO][H_2O]}) \tag{2.8}$$

Where, D is the diffusion coefficient for CO. In catalyst with small pore radius, of the order of 20 Å, the transport of material at atmospheric pressure is independent of total pressure.

For ICI 52.1 Low Temperature Shift conversion catalyst, the following expression has been derived:

$$\frac{d(G[CO_2])}{dV} = \frac{523.15}{T} \cdot \frac{K_L[CO][H_2O]^{1/2}}{\frac{1}{P}+K_A[CO]+K_B[CO_2]}(1-\frac{K}{K_p}) \tag{2.9}$$

Where,

$$K_L = K_{LS}\exp\left[\frac{E_{LS}}{R}(\frac{1}{T_{LS}}-\frac{1}{T})\right]$$

$$K_A = K_{AS}\exp\left[\frac{E_{AS}}{R}(\frac{1}{T_{AS}}-\frac{1}{T})\right]$$

$$K_B = K_{BS}\exp\left[\frac{E_{BS}}{R}(\frac{1}{T_{BS}}-\frac{1}{T})\right]$$

Where, K_{LS}, 68443 moles CO_2/sec/atm (abs)/m^3, is the standard activity for one year old catalyst. K_{AS}=4.31 atm^{-1} and K_{BS}=1.35 atm^{-1}

E_L is the activation energy and

$$\frac{E_L}{R} = -3620K$$

$$\frac{E_{AS}}{R} = -4580K$$

$$\frac{E_{BS}}{R} = -1500K$$

T_{LS}, T_{AS} and T_{BS} are standard temperature, all at 513.15 K; K_{AS}, K_{BS}, E_{AS} and E_{BS} are constants in the rate equation determined from the experimental data. These rate equations cannot be integrated analytically but are integrated numerically using Simpson's rule.

The rate equation for CCIFE (Catalysts and Chemicals Inc., Far East) low temperature shift catalyst C18 may be expressed as given below in the case of higher partial pressure of steam.

$$r = K\left(1 - \frac{X_{CO}}{X_{eqCO}}\right) \tag{2.10}$$

Where,

$K = \exp\left[12.88 - \frac{3340}{T}\right]$, T is in °R.

$$X_{eqCO} = \frac{CO_{in} - CO_{eqOut}}{CO_{in}}$$

CO_{in}: moles of CO at the inlet

CO_{eqOut}: moles of CO at the outlet at equilibrium.

r = reaction rate, moles/mass of catalyst/time

2.3 INFLUENCE OF OPERATING VARIABLES ON SHIFT REACTION

Temperature: Maximum and minimum operating temperatures are restricted from avoiding sintering of copper and dew point of process stream. Equilibrium becomes more favorable with decreasing temperatures; on the other hand, rate of reaction increases with temperature. Industrial operating temperature remains in the range of 180-250°C.

Pressure: Generally activity of catalyst increases with the increase of pressure. For LTS catalyst, the activity appreciation does not level off at pressure up to 500 psig. However, pressure does not affect thermodynamic equilibrium.

Flow Rate: Decreasing the flow rate, for a fixed catalyst volume, results in a closer approach to equilibrium and a conversion of a greater percentage of the CO in the feed.

Steam/Dry gas ratio: Increasing the steam to dry gas ratio results in a lower equilibrium CO and a decrease in contact time.

Catalyst Size: Activity is affected by the geometric surface area, decreasing the size of the catalyst will result in an increase in the reaction rate. For an operating plant with a fixed catalyst volume, it is possible to increase capacity resulting additional pressure drop. In the case of CO converter systems, pressure drop is relatively low.

All catalysts experience a decrease in surface area with the time. The loss in surface area results in a decline in catalyst activity. The rate of decrease in surface area increases with an increase in temperature. It is, therefore, desirable to operate a CO conversion system at the minimum temperature attainable within the design heat balance that will give the desired CO conversion. Effective catalyst life decreases if improper heat exchangers and controller are used. The ability of the plant operator to operate his plant with a minimum of temperature upsets will contribute to efficient utilization of CO conversion catalysts.

2.4 CATALYSTS FOR LOW TEMPERATURE SHIFT (LTS) REACTION

As mentioned earlier, industrially, LTS reaction is catalyzed by Fe_2O_3-Cr_2O_3 catalyst at high temperature and Cu-based catalyst at low temperature. But many other metals and metal oxides as well as recently reported homogeneous catalysts catalyze this reaction. This section of the literature review will focus on the on going research on conventional LTS catalysts and development of its alternative.

2.4.1 Cu Based LTS Catalysts

LTS catalysts have been commonly based on CuO/ZnO although Al_2O_3 is normally also present in commercial catalysts. Typical properties of the commercial LTS catalysts used in the fertilizer industries of the world are shown in the Table 2.1 (Begum, 1992).

Table 2.1: Typical Physical and Chemical Properties of Commercial Low Temperature Shift Catalysts

Catalyst Type	**C18-1**	**C18HC**
Physical Properties		
Catalyst Form	Tablets	Tablets
Catalyst Size(Nominal),inch	1/4 x 1/8	1/4 x 1/8
Bulk Density, kg/l	1.120±0.80	1.280± 0.80
Side Crush Strength, kg	5.6	5.6
Chemical Properties		
CuO wt% (Calcined Base)	25	42±2
ZnO wt% (Calcined Base)	Balance	Balance
Al_2O_3 wt%(Calcined Base)	22	22

Preparation and characterization of very active copper-zinc oxide and Cu/Zn/Al oxide low temperature shift catalysts using a single phase copper –zinc precursor compound were studied by Petrini and Montino (1983). From characterization and activity results, it is inferred that under reaction conditions, a free Cu (I) containing phase is the active phase. The activity of the binary catalyst is maintained when the Al component is added successively while co-precipitation gives a less active catalyst.

The activity and structure –sensitivity of the WGS reaction over Cu-Zn-Al mixed oxide catalysts were observed critically by Gines et al. (1999). They prepared three sets of samples with different Cu/Zn and (Cu+Zn)/Al atomic ratios by co-precipitation. The prepared ternary hydroxyl-carbonate precursors containing hydrotalcite, aurichalcite and/or rosasite phases were decomposed to obtain CuO, ZnO, $ZnAl_2O_4$, and Al_2O_3 in the precursors. After activation with hydrogen, samples were tested for the LTS reaction at 503 K. The turnover frequency of the eighteen samples tested was essentially the same (0.2-0.3 s^{-1}) irrespective of changing the copper metal surface area between 3 and 35 m^2/gm Cu and the metallic copper dispersion between 0.5 and 5.0%. This indicates that the LTS reaction is a structure-insensitive reaction, as the specific reaction rate is always proportional to the copper metal surface area. It was found that the value of the metallic copper dispersion is related to the amount of hydrotalcite contained in the hydroxyl-carbonate precursor: the higher the hydrotalcite content in the precursor, the higher the copper metal dispersion in the resulting catalyst and, as a consequence, the higher the catalyst activity. Ternary $Cu/ZnO/Al_2O_3$ catalyst exhibited a substantially faster LTS activity than binary Cu/ZnO catalysts.

Ghorai et al. (1981) has observed that the surface properties of ZnO have a considerable effect on the dispersion and surface properties of copper. In his work, attempts have been made to correlate the surface properties of the active component to the activity of the catalysts. The reaction was proved to be facile. It was also observed that pores in the range of 4-300 Å have a significant effect on the activity of the catalysts.

Ochida et al.(1967) found that active alumina-copper catalysts could be produced by kneading coke with alumina powder with high specific surface area. It has been shown by Gupta et al.(1981) that the surface area or effective surface area does not bear any relation to the activity of the low temperature shift catalyst. However, the activity increases with the effective copper surface area.

To observe the transformation of Cu^0 to Cu^{2+} and active surface formation, catalyst containing 30-100% Cu obtained by leaching Cu-Zn-Al and Cu-Zn alloys and with oxides of the CuO-ZnO system containing 5-20% CuO was studied by Trcheimnov and Sobolvski (1990). The precursors of the active phase are honeycomb and oxide catalysts are Cu-Zn-Al clusters in which Zn served as a stabilizer of the cluster surface. The active surface was formed during steam conversion of CO as a result of the transformation Cu^{o} to Cu^{2+}.

The catalytic activity and physico-chemical properties of a series of copper catalysts prepared with various supports like ZnO, MgO, Al_2O_3 and SiO_2-Al_2O_3 have been measured by Chaudhuri et al (1986). During their study, it is found that the dispersion and distribution of copper depend mainly on the structure of the support. The surface of copper, the copper metal area and the reducibility and crystal size of copper have been determined and attempts have been made to correlate them with catalytic activity. It is observed that ZnO is the best support in comparison to others.

Saito et al. (2003) also studied that the activity of $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst for the water gas shift reaction at 523 K was less affected by the pre-treatments such as calcinations and treatment in H_2 at high temperatures than that of $Cu/ZnO/Al_2O_3$ catalyst. The $Cu/ZnO/ZrO_2/Al_2O_3$ is also highly active for the water-gas shift reaction at 673 K. Furthermore, a two-stage reaction system composed of the first reaction zone for the water-gas shift reaction 673 K and the second reaction zone for the reaction at 523 K was found to be more efficient than a one-stage reaction system. The addition of a small amount of colloidal silica to a Cu/ZnO-based catalyst greatly improved its long-term stability in the water-gas shift reaction.

The effect of calcination temperature on the activity and some properties of low temperature water gas shift reaction catalyst have been reported by Sohrabi and Irandoukht (2003) and Begum (1992). The activities of catalysts have been determined using a fixed bed catalytic reactor. They summarized the following outcomes:

- The catalysts total surface area decreased with increasing calcination temperatures, presumably due to the partial sintering of the catalysts particles.
- The presence of an amorphous CuO phase within the structure of some catalysts may be related to the desirable conditions prevailing during synthesis of the latter.

- Copper crystallite particle size and enhancement of catalyst activities with increasing calcination temperatures demonstrate the important contribution made by the copper crystallite phase to the overall activities of water gas shift reaction catalysts.

All commercial catalysts for water-gas shift reaction in the low temperature region contain zinc oxide in addition to the main active component, copper. Different benefits of zinc oxide are closely observed by Spencer (1999). He observed that the formation of zincian malachite and other copper/zinc hydroxy carbonates is essential in the production of small, stable copper crystallites in the final catalyst. Further, the regular distribution of copper crystallites on the zinc oxide phase ensures long catalyst life. Zinc oxide also increases catalyst life in the water-gas shift reaction process by absorbing sulfur poisons but it is not effective against chloride poisons. On the other hand, Saito, M. et al. (2004) have observed that the specific activity of the supported Cu-based catalyst for water-gas shift reactions was not improved by the addition of ZnO to the catalyst. The catalyst activity could be correlated mainly to the Cu Surface area of the catalyst.

The water-gas shift reaction, on industrial Cu-based catalysts, has been investigated by Hakkarainen and Salami (1989) by the transient kinetic, chemisorption, thermo-gravimetric and photoelectron spectroscopic methods. A significant reduction of the catalyst and increase in the surface area were observed during the initial activation at 250°C. The presence of reduced surface Cu was confirmed by photoelectron spectroscopy. The studies of stationary water-gas shift kinetics at 200-250°C revealed that the reaction order with respect to CO and H_2O is less than 1. The transient stage started after exposure to N_2 showed that the CO_2 response was faster than the H_2 response at 250 and 235°C, whereas, at 150 and 200°C the CO_2 and H_2 liberation rates were almost equal. The CO_2 and H_2 formation rates were enhanced by H_2O and H_2O-H pretreatment of the catalyst. A reaction mechanism based on the kinetic studies and the catalyst properties is discussed. The mechanism includes both catalyst oxidation-reduction and bimolecular surface reaction steps.

Some cases, addition of small amount of other component to the conventional Cu-based catalyst changes properties of catalyst significantly. For example: addition of Manganese (Mn), the effect of Manganese (Mn) on catalytic activity of Cu-Zn-Cr catalyst in LTS reaction by using co-precipitation catalyst containing 1-6% Mn was studied by Jovanovic et al.(1988). Conversion increased with Mn concentration and reached a maximum activity and highest thermal stability at 3 and 4% Mn (with 97.9% conversion yield).

2.4.2 Development of Alternative Low Temperature Shift (LTS) Catalysts

Recently, researchers are trying to find out active and stable alternative catalyst for WGS reaction mainly for small-scale use in fuel cell power generation. This section of literature review will discuss some of the approaches.

To find stable and active catalyst, Flytzani-Stephanopoulous et al. (2001) have made fundamental research on novel Cerium Oxide based catalyst for WGS reaction and integration of this catalyst with Pd-alloyH_2-separation membranes supplying high purity hydrogen for fuel cell use. They prepared a series of nanostructured Cu and Fe containing Ceria catalysts by a special gelation/precipitation technique followed by air calcinations at 650°C. They reported Cu-Ceria as the most promising shift catalyst for integration with H_2-selective membranes. The specific formulation 10at%Cu-C10L is both highly active and stable, Figure 2.1, in operation at 450°C and in CO_2-rich or H_2-rich gas streams.

The catalyst, referred to as Selectra Shift, activates in process gas, has stable activity under a wide variety of process conditions and is safer if accidentally exposed to air. It, therefore, represents a safer alternative to the commercial Cu-Zn. W. Ruettinger et al.(2003) have developed a base metal non-pyrophoric alternative to commercial Cu-Zn named Engelhard Selectra Shift Particulate WGS catalyst having small activity loss in water exposure and thermally stable up to 350°C with high catalytic activity and stability. They have generated the curve shown in the Fig. 2.2 to test the stability of Selectra Shift catalyst under operating environment. In this test, the catalyst was repeatedly cooled to 60°C to condense a limited amount of water on the catalyst. After each low temperature exposure, the catalyst was heated to 200°C and 250°C to test its activity.

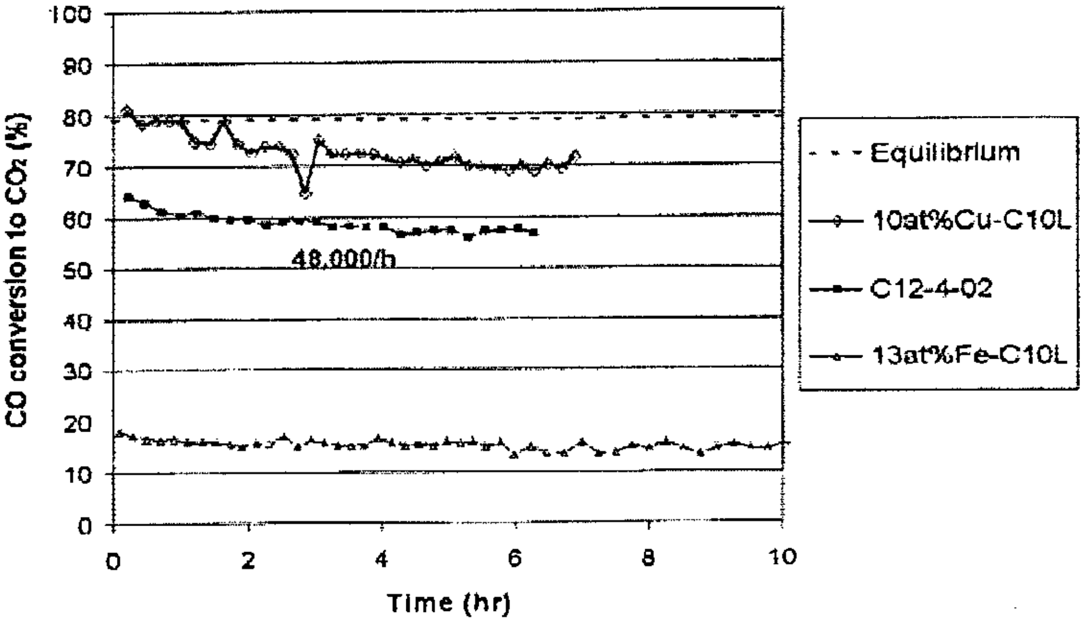

Fig.2.1 WGS activity / Stability in a Simulated Coal-Gas Composition, 10%CO-34%H_2O-10%CO_2-15H_2-He, 450°C, S.V.=80,000 h^{-1}

Supported gold catalysts that were already known to exhibit very high activity for the CO oxidation as Au/TiO_2, Au/Fe_2O_3 and Au/CeO_2 have proven to be also active LTS catalysts. This catalyst also includes oxides of Cobalt plus Cr_2O_3 along with Cu and Zn.

The composite system of nano-structured gold and cerium oxide, with a gold loading 5-8%, is reported in as a very good catalyst for low temperature shift reaction. Activity depends largely on the presence of nanosized ceria particles. Fu, Q. et al. (2003) have also shown that nanometallic Au species strongly associated with surface Ce-O groups are responsible for the activity.

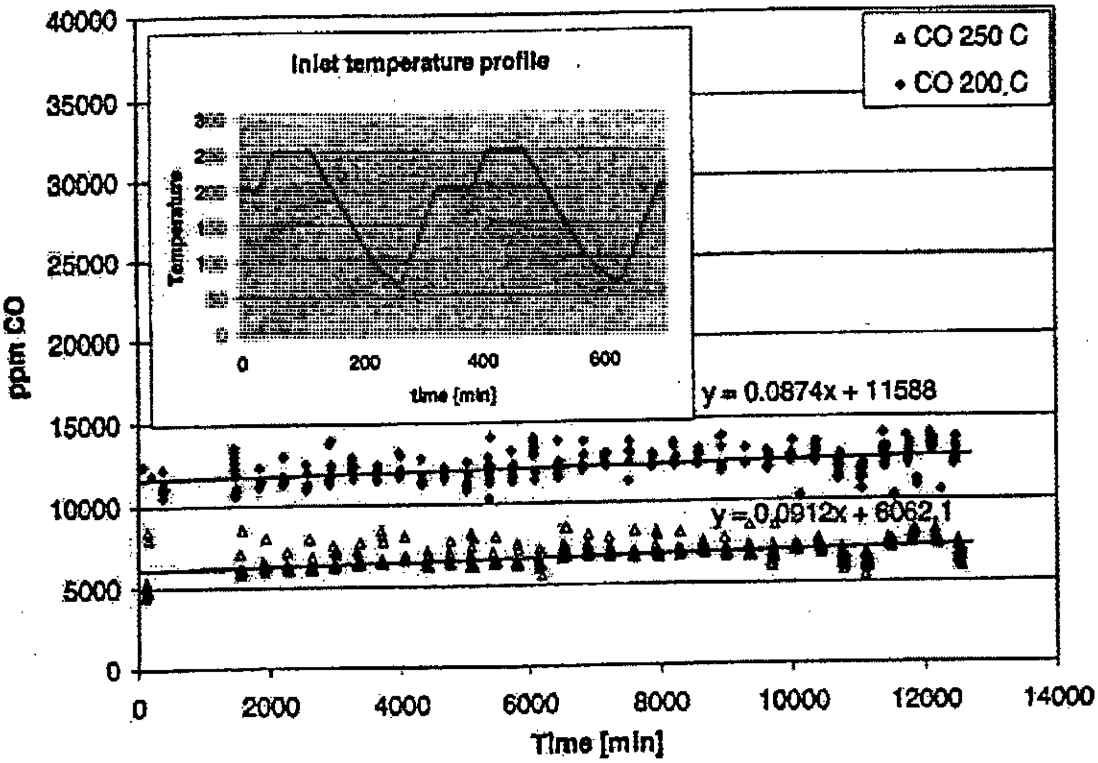

Fig. 2.2: Stability of Selectra Shift towards Condensing Water

Molybdenum Carbide (Mo_2C) has been proven as highly active catalyst for LTS reaction of a synthetic steam reformer exhaust stream. This catalyst is more active than a commercial Cu-Zn-Al shift catalyst under the conditions of 220-295°C and atmospheric pressure. In addition, Mo_2C did not catalyze the methanation reaction. Patt et al. (2000) have studied also the deactivation behavior of Molybdenum Carbide catalyst. They have observed no apparent deactivation or modification of the structure during 48 hrs on stream.

Douglas et al. (1983) conducted a comparative study of catalytic material for the water-gas shift reaction in pressurized aqueous system, i.e. a homogenous system. Results of this investigation have shown that alkali metal salts catalyze the water-gas shift reaction in the temperature range of 200-400°C. Alkaline earth salts were found to be significantly less active. Transition metal salts ranged in activity from better than the alkali metals in some cases to nearly as poor as the alkaline earths in other cases. The use of ammonia and ammonium compounds was also demonstrated. Experimental results show that dissolved alkali catalysts compare favorably with slurried conventional supported metal oxide catalysts in the pressurized aqueous system.

2.5 REDUCTION OF LTS CATALYSTS

LTS catalysts consist of copper and zinc oxides, plus aluminum, or other oxides. Only the copper oxide is reduced and the reactions that can occur are:

	Heat of reaction at 25°C, kcal/mol	
1. $CuO + H_2 = Cu+H_2O$	19.30	(2.11)
2. $CuO+CO = Cu+CO_2$	29.13	(2.12)
3. $2Cu + O_2 = CuO$	77.00	(2.13)
4. $ZnO + CO_2 = ZnCO_3$	15.49	(2.14)

The reduction kinetics of a copper based LTS catalysts were studied by Desheng and Shulan (1983) in a microreactor at atmospheric pressure by a flow method. The reaction mechanism is different from that of pure CuO. No induction period is observed when the temperature is less than 443 K. In temperature programmed reduction curves, despite the temperature and high pressure involved, the peak always appears at the same place where the reduction of the catalyst reaches a certain degree.

The change in the relative content of the elements on the surface of the catalyst during its reduction was determined by Chudinov during his study. The method of X-ray photoelectronic spectroscopy (XPES) was used to investigate the reduction of oxides of copper and a Cu-Cr-Zn-Al catalyst in H_2 in the range of 50-400°C. It was shown that the reduction of the CuO to metallic copper proceeds partially through the formation of Cu_2O when a Cu-Cr-Zn-Al catalyst is reduced in H_2 in the range of 170-300°C. The relative amount of Copper (II) oxides and metallic copper on the surface of the catalyst increases linearly.

Duan et al. (2004) studied the reduction kinetics of CuO/ZnO/Al2O3 catalyst using Temperature Program Reduction (TPR) technique. It has been found that under normal reduction conditions only CuO is reduced and the extent of reduction increases with that of dispersion. Literature review on reduction reveals that at 220°C, the equilibrium constants for reactions 2.12 and 2.13 are 10^{12} and 10^{41} respectively, so that metallic copper is the stable state under normal operating conditions. The heat of reduction of LTS catalyst containing 30 to 35% CuO by hydrogen is about 80,000 Kcal per 1000 kg, equivalent to a temperature rise of 450°C. Carefully controlled reduction is therefore required since the catalyst surface sinters above 260°C loosing surface area and activity. To prevent the loss, catalyst is reduced by heating up slowly in a low concentration of hydrogen so that the temperature rise can be controlled by the heat capacity of the carrier gas and the rate of admission of hydrogen to the catalyst.

2.6 DEACTIVATION AND REGENERATION OF LTS CATALYSTS

The most catalysts used in heterogeneous catalytic processes are subject to a decrease in the initial activity over a period of time. The 'life' of a catalyst may be defined as the period during which the catalyst produces the required product at a yield equal to or greater that originally specified. For most catalysts, the activity declines sharply at first and then reaches a state where the catalyst activity decreases much more slowly with time. Reasons for catalyst deactivation are: particle failure, fouling, component volatilization, phase changes, compound formation on catalyst surface, sintering, poison adsorption and coking. Following four factors are mostly important for the deactivation of LTS catalysts:

- Increase in the dimensions of the copper crystallites
- Poisoning by sulfur
- Poisoning by chlorine
- Effect of condensates

The crystal growth of copper may take place when the catalyst is in service for the thermal sintering. Improper H_2-reduction methods and steam reduction result in lower LTS catalyst activity. Sulfur is the most common and widely known LTS catalyst's poison. As an estimate, 0.3 %(wt) deposition of sulfur on the catalyst would deactivate it significantly.

Condensation of water on to the catalyst can be harmful under different circumstances:

1. Condensation in the presence of process gas reduces the copper active surface.
2. In cases where the upper part of the catalyst has been wholly or partially poisoned by chlorine, the chlorine is washed down into the lower part of the bed by the condensate. The lower part of the bed is thus in turn deactivated.

Regeneration of Cu-Zn-Cr and Cu-Zn-Al heterogeneous catalysts, deactivated by sulfur and chlorine compounds, was studied by Magdziarz et al. (1978). The method consists of oxidation of the catalyst in N_2 or steam atmosphere, where the amount of O_2 is controlled so that the temperature in the catalyst bed remains less than 240°C. After oxidation, a flow of air or steam is directed through the catalyst bed at 200-240°C for 16-24 h. After cooling, the catalyst is washed with deionized water at 70-100°C, dried and reduced in the usual way. The flow of gases and water during the regeneration process is in the reverse direction compared to the flow of the process gas. After regeneration, the catalyst exhibited less than 90% of the initial activity.

2.7 CATALYST PREPARATION METHODS

2.7.1 Laboratory Methods

A number of laboratory methods are known for the preparation of supported $CuO/ZnO/Al_2O_3$ systems. The widely used methods are:

1) **Incipient Wet Impregnation Method:** In this method, the support is soaked in a solution of active metal salt. The pores of the support get filled and a deposit of the salt on the support is obtained. After drying, the sample is decomposed to get a supported metal oxide catalyst and the oxide catalyst is reduced in an atmosphere of hydrogen at a suitable temperature to get the desired supported metal catalyst. The concentration of the metal can be increased carrying out successive impregnations. Usually the metal content is calculated from the concentration of salt solution.
2) **Adsorption from Solution:** In this method, the porous support slowly added with continuous stirring to a solution containing active metal compound. Capillary forces draw the liquid into the pores with a pressure of several hundred atmospheres. The active components are adsorbed on the walls of the pores. The resulting sample prepared by this method may contain varying distribution of metal oxide and metal on the support depending on the method of mixing the support, the strength of the solution, contact time, metal distribution, metal dispersion etc.
3) **Deposition:** The preformed metal or one of its oxides is deposited from suspension onto a suspension of the support. This method offers considerable opportunities for controlling the size and shape of the metal particles.
4) **Precipitation:** This method involves the addition of a precipitating agent leading to the formation of a homogeneous hydroxide precipitate of the active metal on the support. At a definite temperature, the precipitating agent generates OH^-, which converts the active metal salt solution to hydroxide and a magnetic rotor helps to precipitate it on the support homogeneously. After separation and drying, the sample is decomposed to supported metal oxide catalyst and the catalyst is reduced by hydrogen at an appropriate temperature

to supported metal catalyst. The concentration of the metal can be increased by carrying out successive precipitation or by using higher concentrated active metal salt solution. The resulting catalyst may contain varying distribution of metal on the support depending on the area of the support, the strength of the active metal salt solution, the speed of rotation of the stirrer, the time of stirring etc. This method is an effective method in preparation of the supported catalyst and can be performed easily under available laboratory facilities.

5) **Co-precipitation:** This method involves the addition of a precipitating agent leading to the formation of a mixture of metal compound and support, both previously in solution. This method is traditionally associated with nickel-silica catalysts used mostly in the hydrogenation of unsaturated fatty oils. At a definite temperature the precipitating agent generates OH^- ions that convert the active metal salts to a mixture of metal hydroxides. After drying, the sample is decomposed and reduced to get a co-precipitated supported catalyst. This method offers a better surface in terms of homogeneity, though some of the active component may be embedded within the carrier and hence not available for reaction.

2.7.2 Commercial Method

Finished product of Cu-Zn-Al catalyst is usually in the oxide form. The active ingredient in all LTS catalysts is the copper, which must be present in the form of small crystallites. Zinc oxide and alumina are used as spacers or inhibitors; that is, they inhibit the growth of copper crystals. Therefore, to be effective the zinc and/or alumina must be co-precipitated with the copper.

Starting raw materials for LTS catalyst can be any number of soluble Copper & Zinc salts, including sulfates, nitrates, and chlorides, among others. Alumina is normally obtained by the addition of Sodium Aluminates.

The first step in the production of an LTS catalyst is placing into solution the soluble copper, zinc, and alumina salts. Usually the zinc and copper salts are placed in solution in one tank, and the alumina solution is made in a separate tank.

Solution of the copper and zinc salts and the solution of sodium aluminate are then pumped to a precipitation tank containing sodium carbonate. The sequence of addition of the solution to the agitated precipitation tank varies depending upon the manufacturing process. Temperature and pH also vary with the manufacturing process and manufacturer. The co-precipitate of zinc, copper and alumina is then filtered in a plate and frame press. The filter cake is then washed to remove sodium.

After removal of sodium, the filter cake is fed to a continuous belt calciner where it is dried and copper & zinc are converted to the oxides. The calcined oxides are then fed to a granulation mixer where a lubricant is added. The material is then tableted in the desired size and drummed. A typical flow sheet for manufacturing commercial catalysts is given in Fig. 2.3 (Slack, 1974).

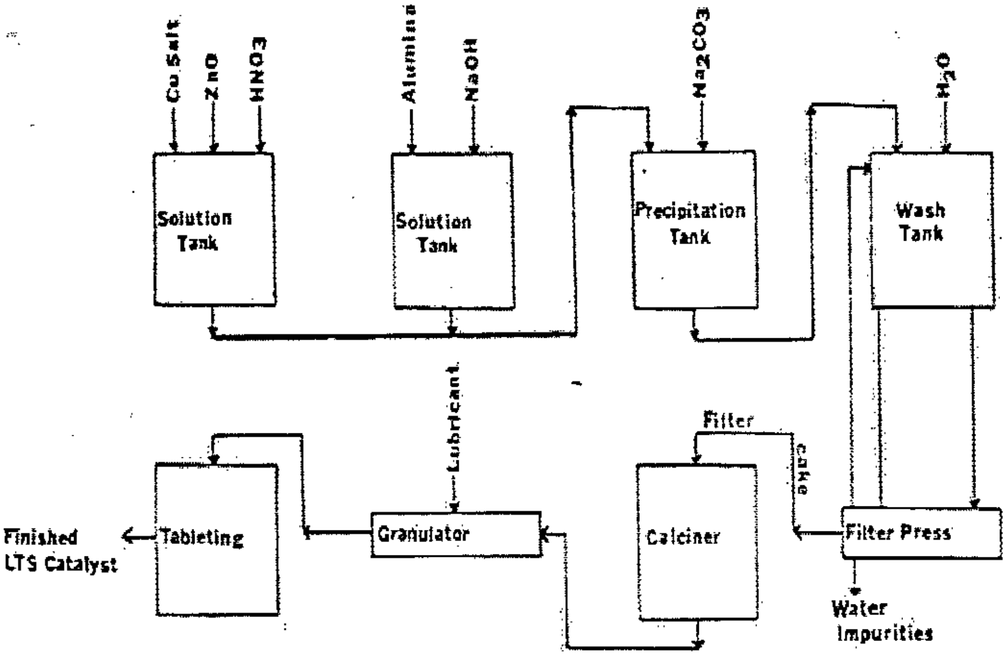

Fig. 2.3: Process for Manufacturing Low Temperature Shift Catalyst

2.8 PHYSICAL AND CHEMICAL CHARACTERIZATION OF HETEROGENEOUS CATALYSTS

Physical characterization includes determination of the total surface area, pore volume, pore size distribution and crystallite size. Besides, Chemical characterization covers the determination of the activity and dispersion of active metal surface area. The Pulse ChemiSorb 2705 of Micromeritics, USA, can be used to measure Langmuir & BET surface area, total pore volume and dispersion of active metal surface area.

2.8.1 BET Surface Area

The measurement of the total surface area of catalyst is most frequently carried out via physical adsorption method. The experimental data are analyzed using BET equation, which can be written as

$$\frac{\frac{P}{P_0}}{V\left[1-\frac{P}{P_0}\right]}=\frac{1}{V_m C}+\left(\frac{C-1}{V_m C}\right)\left(\frac{P}{p_0}\right) \tag{2.16}$$

Where,

V = Volume of gas adsorbed at an equilibrium pressure P

P_0 = Saturation vapor pressure of adsorbate

V_m = Volume of a monolayer of adsorbate

C = Constant

The total surface area is computed from

$$S_{BET}=\frac{V_m N_o A_m}{V_{mol}} \tag{2.17}$$

Where,

N_o = the Avogadro number

V_{mol} = molar volume of the adsorbate

Simple non-polar molecules such as the rare gases or nitrogen are widely used as adsorbate. The standard BET procedure for multipoint surface area requires the measurement of at least three and preferably five or more points in the appropriate pressure range on the N_2 adsorption isotherm at the normal boiling point of liquid nitrogen.

2.8.2 Total Pore Volume

The scientist, Gurvitsch (Operator's Manual, 1994) noted many years ago that the volume of liquid condensed in the pores of a porous solid from a condensable gas near its saturation vapor pressure is equivalent to the volume of the pores. This finding is now generalized into the 'Gurvitsch Rule' and restated to apply typically at 0.95 relative pressures, a mass of data having accumulated confirming the general validity of the rule. A total pore volume measurement with the Pulse Chemisorb 2705 thus requires determining the volume of gas which, condensed as a liquid, is extracted by a sample from a 95-98 % N2/ 5 % He gas mixture at liquid nitrogen temperature.

It must be noted that this technique, as well as all other gas-based measures of pore volume, does not distinguish between the gas condensed within pores and that adsorbed on surfaces external to the pores. The assumption is merely made that the adsorbed gas quantity is small relative to that condensed. Such an assumption is quite good with moderately-to-highly porous catalyst and adsorbent that is the primary materials for which pore volume is an important physical property.

2.8.3 Dispersion of Active Metal Surface Area

Density of active sites, called the dispersion, on heterogeneous catalyst surface can be measured by chemisorption measurement. Heterogeneous catalyst dispersion is especially important in the economics of any catalytic process. If sufficient site density, or dispersion, is attained with the lesser value, then the catalyst cost is essentially one-half what it otherwise would be. Dispersion information is also of great importance to any scientist wishing to follow the kinetics of a catalytic reaction. The number of active sites as measured with different gases gives a relative measure of the activity of a catalyst for different reactions.

Dispersion , D, is the ratio of active metal atoms exposed on the catalyst surface N_{Active} to the total number of metallic atoms incorporated in the catalyst N_{Total}, i.e,

$$D = \frac{N_{Active}}{N_{Total}} \tag{2.18}$$

Chemisorption testing reveals N_{Active}. The totality of metal atoms N_{Total} has to be computed from the knowledge of the mass of metal incorporated in the catalyst.

Chapter 3

EXPERIMENTAL

Experimental methodology for preparation, calcination, reduction and physical and chemical characterization of LTS catalyst are described in this chapter. Flow diagrams, Schematic diagrams and detail drawings are used to facilitate the understanding of the experimental set up.

3.1 PREPARATION OF CATALYSTS

Four different methods (Method 1, Method 2, Method 3 and Method 4) were used to prepare the catalysts following co-precipitation, chemical mixing, and impregnation principles. The quantity of catalyst prepared at a time was 25 gm. The tablets of calcined catalyst particles (<200 mesh) have been prepared with the help of a hand press and the required catalyst particle size used in activity testing was prepared by crushing and sieving those tablets. The catalysts were prepared under atmospheric pressure. The salient features of the methods used during this study have been described in the following sections:

Method 1(M1): Components of catalyst were dissolved in 200 ml of distilled water. To this solution, 7N solution of precipitant potassium hydroxide (KOH) was added drop wise at 30°C at a rate of 5 ml/min with constant stirring until dense precipitate was formed. Then the precipitate was diluted by 700 ml of distilled water. The amount of the precipitant added corresponded to that necessary to have a final pH after neutralization of about 7. After that the precipitate was divided into three portions and washed each portion thrice taking 1 liter distilled water at a time. The washed precipitate slurry was kept for 24 hrs under laboratory conditions. The precipitate was then filtered and dried for 5 hrs at 150°C and 230 mm Hg pressure.

Method 2(M2): Solution of the catalyst components was prepared using 20-25 ml of distilled water at 30°C and then dried for 7 hrs at 115°C and 230 mmHg pressure. Keeping under laboratory conditions for 16 hrs, the slurry was calcined in air at 225-400°C with constant stirring for two hours.

Method 3(M3): The support Particles (16-32 mesh activated γ-Al_2O_3) were suspended in a highly concentrated aqueous solution of salt of catalyst components for a period of 10 mins. Then the slurry was dried at 115°C and 230mmHg pressure for 7 hrs. Then the dried material was kept for 16 hrs under laboratory conditions. After that the dried catalytic material was calcined in air at 225-400°C with constant stirring for two hours. 20 ml of distilled water were used for dissolving the catalyst components.

Method 4 (M4): The nitrates of Copper and Zinc were dissolved in 20 ml of distilled water. γ-Al_2O_3 (3gm) was then mixed with this solution and calcined in a burner for 3 hrs. The maximum temperature attained during this operation was 260°C.

3.2 CALCINATION PROCEDURE

The calcination of the prepared catalysts was conducted under nitrogen (Method 1) or air (Method 2, Method 3 and Method 4) at atmospheric pressure. In the case of the catalyst prepared by Method 1, the dried catalyst was kept in a glass tube and heated up to the required temperature under slow stream of oxygen-free nitrogen. The temperature of the furnace was controlled with the help of temperature controller. Calcination under normal atmospheric conditions was carried out in a porcelain basin placed on a burner with constant stirring by glass rod. Experimental arrangements used for calcinations under nitrogen is shown in Fig. 3.1

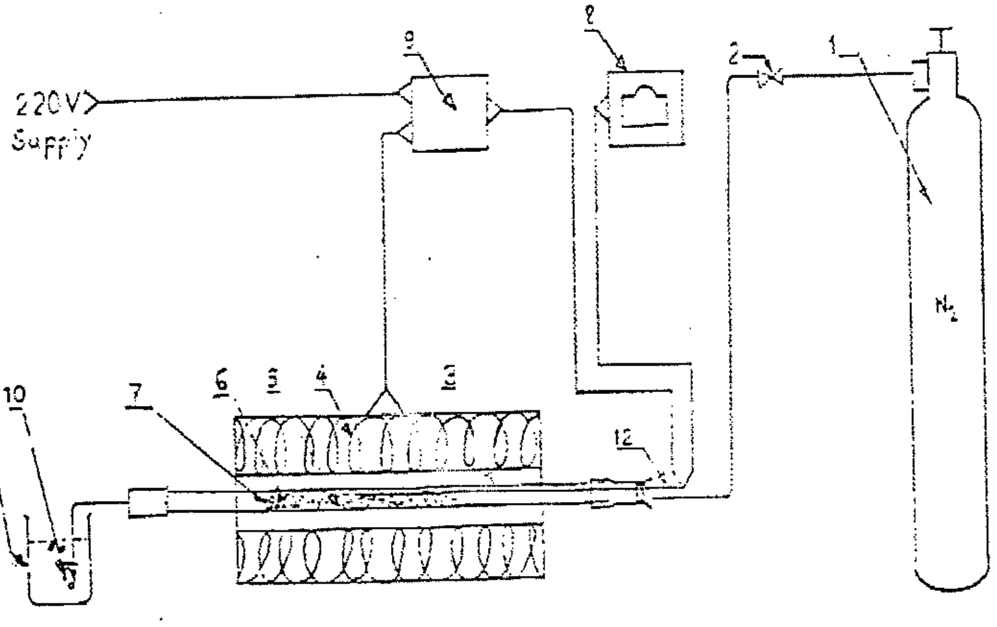

Fig. 3.1 Flow Diagram of the Calcination Section; 1=Nitrogen gas cylinder, 2= Flow control valve, 3=Glass tube, 4=Heating coil, 5= Catalyst on Calcinator, 6= Alumina particle, 7= Stainless steel net, 8= Milivolt meter, 9=Temperature controller, 10= Bubble out of nitrogen oxide, 11=Water beaker and 12=Thermocouple

3.3 EXPERIMENTAL SYSTEMS FOR CHARACTERIZATION OF CATALYSTS

Surface area and pore volume were measured using physisorption measurement in the **Pulse ChemiSorb 2705** of Micromeritics, USA. The front and right side panels of the Pulse ChemiSorb 2705 are shown in the Fig. 3.2. Fig. 3.3 is the schematic diagram of the Pulse ChemiSorb 2705. All operating controls, except power switch, are on the front panel. Utility connections are on the lower right panel and exhaust ports are on the left panel. The Pulse ChemiSorb 2705 provides an economical means for conducting either chemisorption or physisorption tests. Attaching the

TPD/TPR 027 options for the Pulse ChemiSorb to the unit permits it to perform temperature programmed desorption, reduction, and oxidation analyses. This instrument was calibrated according to the procedure supplied by the company.

Before physisorption measurements for the determination of total surface area, pore volume and active metal surface area the catalyst sample was adequately degassed. This was accomplished by flushing the samples with an inert gas at an elevated temperature. Heating to the highest temperature consistent with the thermal stability of the sample was used to expedite degassing. For physisorption measurements the mixture of nitrogen and helium in varying proportions were used. Prior to any measurement, the catalyst sample was dried and weighed.

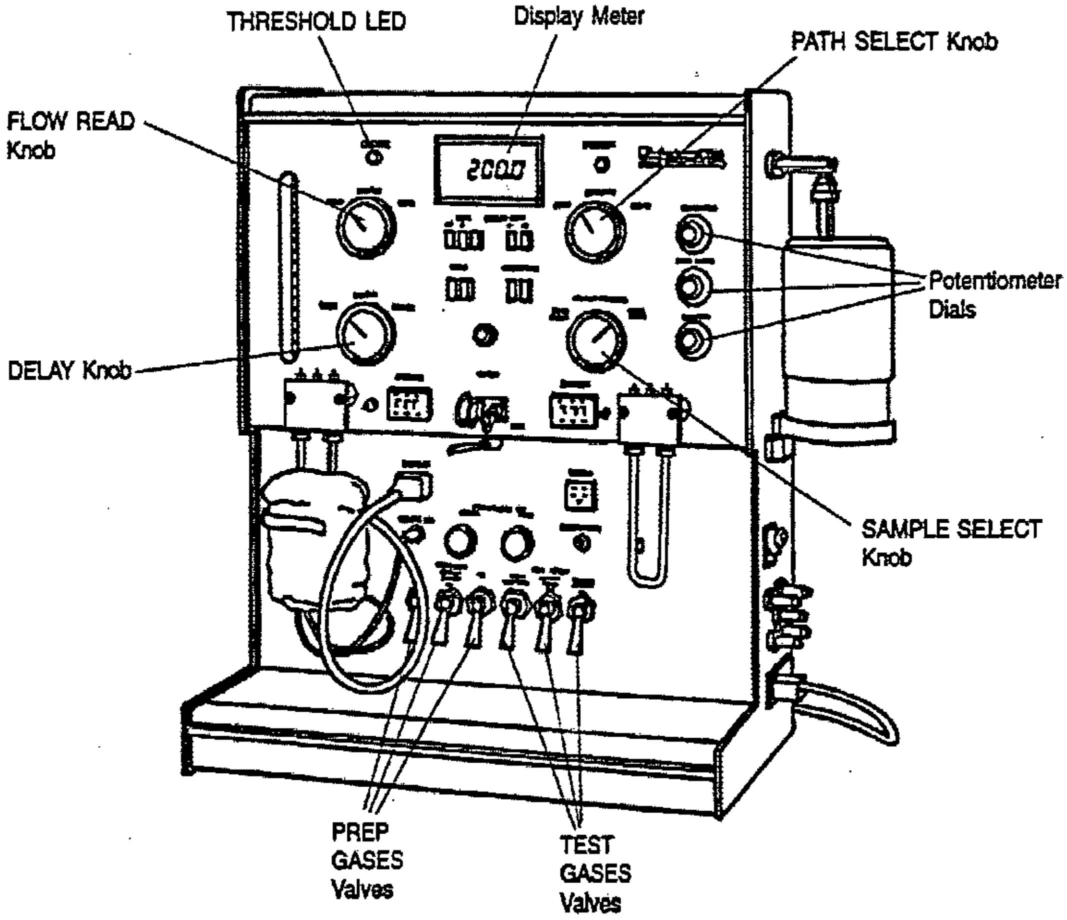

Fig. 3.2: Pulse ChemiSorb 2705

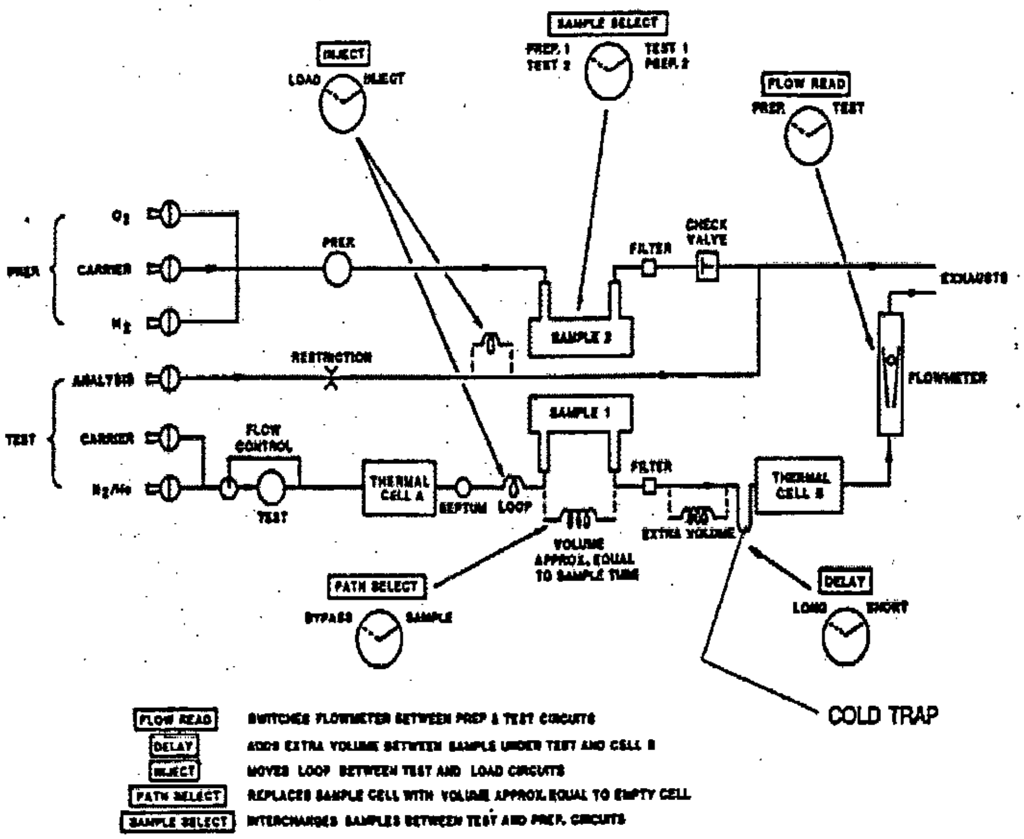

Fig. 3.3: Schematic Diagram of Pulse ChemiSorb 2705

3.3.1 Measurement of Total Surface Area

The BET surface areas were measured using dynamic method of Nitrogen gas adsorption at -196°C employing the **Pulse ChemiSorb 2705.** Both single point and multipoint surface area measurement were used. Single point measurements were accomplished using a 30% N_2/70% He gas mixture. Multipoint analysis was conducted as a series of single-point steps, progressing from lower to higher nitrogen gas concentrations. The concentrations used in our experiment were 15, 30, 50 and 70% N_2 and balance Helium (He). After adequate degassing and drying, sample was transferred to the "test" position. Liquid nitrogen was then placed around the sample to record the adsorption peaks. Desorption peaks were then obtained by removing the liquid nitrogen and bringing the sample to room temperature. Total surface area was then calculated from either the adsorption or the desorption peak.

3.3.2 Pore Volume

To make total pore volume measurements, pure He, pure N_2 and a mixed gas of 95% N_2 and 5% He were used. The volume of gas with which the instrument was calibrated first converted to standard conditions and then to its equivalent liquid volume. The molar volume of liquid nitrogen is 34.67 cm^3 and gaseous nitrogen 22414 cm^3 that is a ratio of 0.00155. Designating the calibrating gas volume by v, the equivalent total pore volume V_{tp} is thus

$$V_{tp} = \frac{273.2}{T_{Room}} \times \frac{P_{atm}}{760} \times 0.00155 \times 100 \times v \tag{3.1}$$

A factor of 100 is included in the computation to permit entry of all significant figures into the instrument. This value of V_{tp} was inserted into the Pulse ChemiSorb as the calibrating factor.

The sample to be evaluated was loaded into the sample attachment unit and was degassed at an elevated temperature. The sample was then cool to near room temperature and exposed to pure nitrogen gas at the temperature of liquid nitrogen for 15 minutes. After waiting for condensation, the flow was then shifted back to 98% N_2, 2% He gas which brought the sample to the desired state of equilibrium at 98% saturation. The total pore volume was then obtained setting the CALIBRATE knob to its appropriate value calculated by equation 3.1 and removing the liquid nitrogen to bring the sample to room temperature. The value displayed was 100 times the sample total pore volume. The displayed number was divided by 100 and the sample weight to obtain the specific total pore volume.

3.3.3 Temperature Programmed Reduction (TPR)

The basic idea of this thermo-analytical technique is to monitor surface reactions of solid catalysts with their gaseous environment by performing a continuous analysis of the gas phase. This technique can provide very interesting results and help toward a better understanding of the system under study, provided that other information, gained from other techniques, is available: for instance, a priori knowledge of the chemical nature and of the state of dispersion of the reactive phase. Here in Pulse ChemiSorb 2705, at first, wet catalysts were used to degas for 1.5 to 2.5 hrs at 150 – 190°C using N_2 gas at a rate of 40 ml/min. Then the degassed catalysts were submitted to a programmed temperature rise up to 750°C, while a reducing gas mixture of 10% H_2 and 90% Ar was flowed over it. The rate of reduction was continuously measured by monitoring the composition of the reducing gas at the outlet of the reactor and temperature vs. time curves were observed using a programmed computer.

3.3.4 Activity Testing Using Tubular Reactor

A Flow diagram of the experimental set up is shown in Fig. 3.4. The apparatus has three main sections:

1. Feed Preparation
2. Tubular Reactor
3. Sampling and Analysis

The reactor system has been designed in such a way that any solid catalyzed gas phase system can be investigated in the reactor.

3.3.4.1 Feed Preparation

The preparation section consists of feed purification and drying, flow measurement, preheating and mixing. All the gases such as CO, H_2 and Ar are supplied from gas cylinders. The purity of the gases as supplied was better than 99.9%. The gases were metered by rotameter, which were calibrated to measure the flow rates of the respective gases using soap bubble flow meter. Mixed reactant gases were then sent through the preheater and tubular reactor. At the same time, steam of 200°C was produced using an electrically heated tube. Water was pumped using microdose-metering pump. The products of the reaction are then passed through the sampling and analysis section.

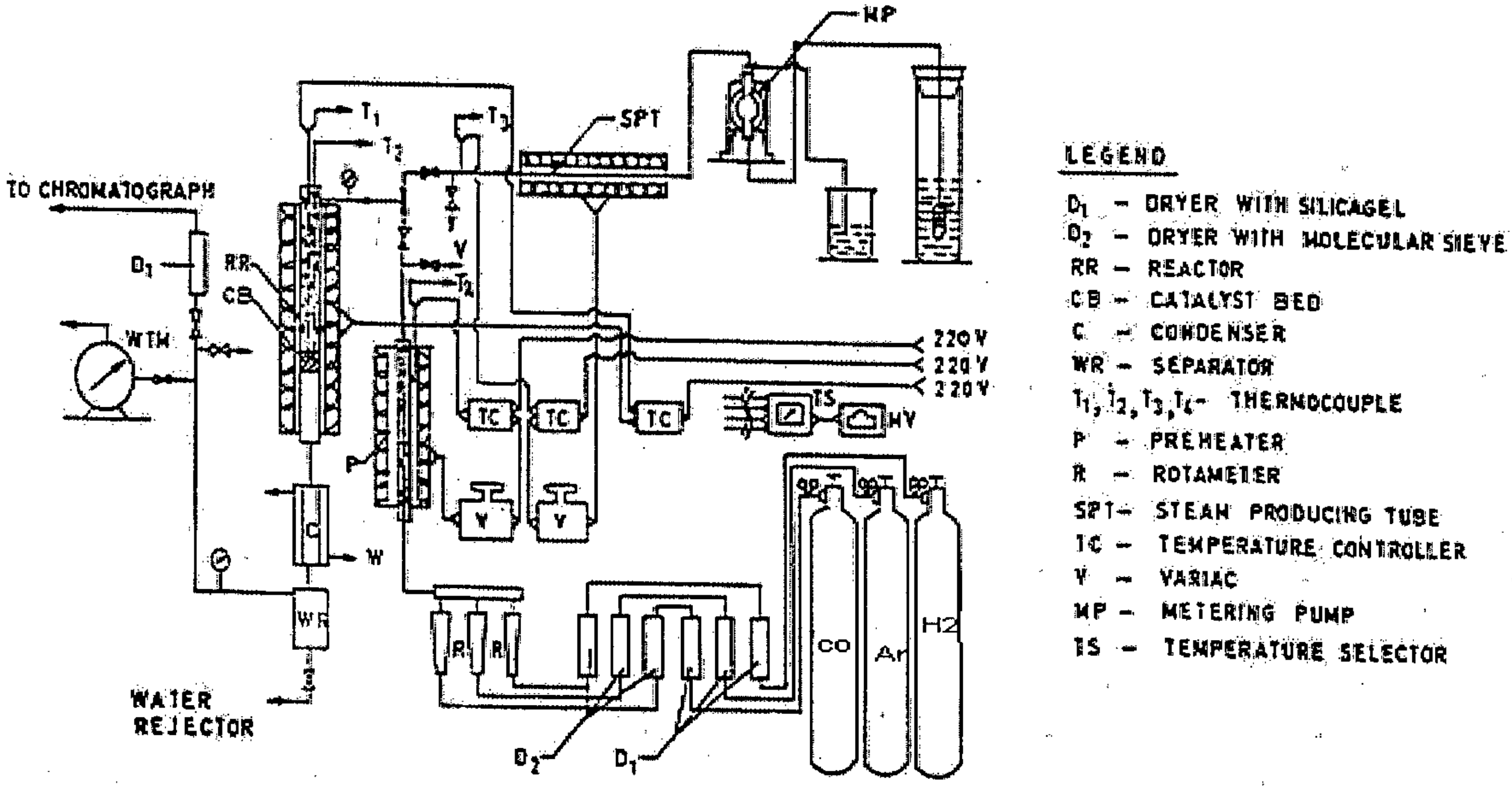

Fig. 3.4: Flow Diagram of Experimental Set-up for Activity Testing

3.3.4.2 Tubular Reactor

The advantage of using tubular reactor for the activity testing is the ease with which any particular reactor tube can be replaced and a reactor tube of different dimensions and containing different catalysts can be introduced. In this work, tubular reactor was installed with temperature controller. Details of the reactor is given in figure 3.5

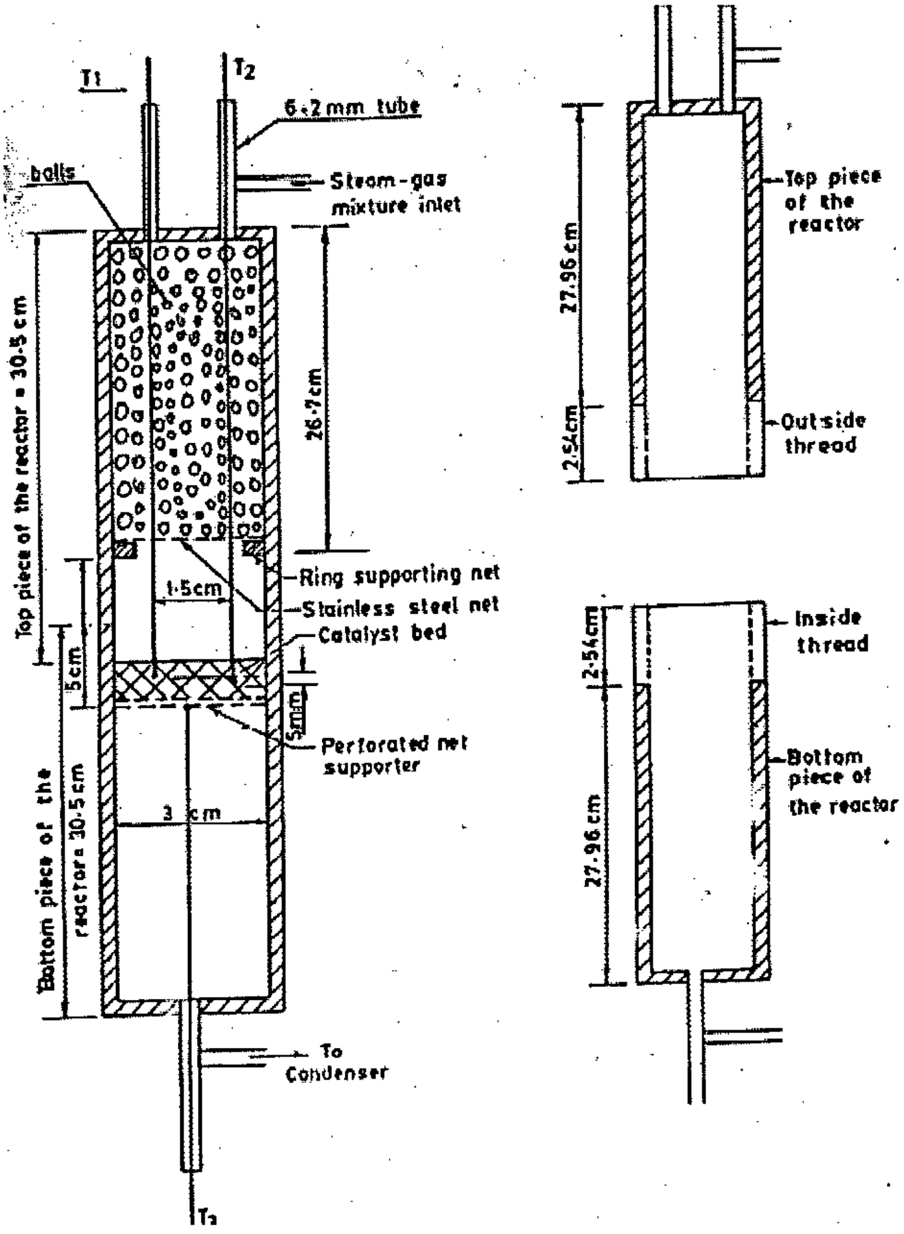

Fig. 3.5: Details of the Reactor for Catalyst Activity and Stability Testing

3.4 SAMPLING AND CHROMATOGRAPHIC ANALYSIS

A Shimadzu model 8C-3A gas chromatograph connected with Shimadzu model R-III recorder and Shimadzu model C-R6A integrator has been used for the analysis of the reactant and product gases. The exit gases from the reactor passed through condensers before being discharged to the atmosphere. A secondary stream is allowed to pass through two columns of silica gel for drying and then sent to the gas chromatograph for on-line analysis of the products. The products were analyzed using two columns; a Porapak Q Column and a Molecular Sieve 5A Column.

Chapter 4

RESULTS AND DISCUSSION

All experiments were performed aiming to enhance and to establish the scientific know-how of catalyst preparation techniques and to find out a possible technique for pilot plant study, which is already proven for laboratory scale study. The experimental set-up and the procedures are described in chapter three. Here, experimental results are presented to explain the performance of the preparation techniques based on activity and stability of the catalysts. The short-term and long-term stability tests are performed only for selected methods and in each case results are compared with industrial catalyst (ICI katalco 83-3). The results of characterization of the prepared and industrial catalysts are presented to support the activity and stability test results.

The results of activity and stability tests are presented in the form of rate of reaction vs. time curves or bar charts. It is to be mentioned here that sample experimental data, sample calculation, calculated data, specification of industrial catalyst and physical property data are presented in Appendix A, B, C, D respectively.

4.1 PERFORMANCE OF LABORATORY SCALE AND INDUSTRIAL CATALYST PREPARATION METHODS

In this investigation, catalysts were prepared using four different methods, which were selected from six different methods studied by Begum, D.A. (1992). Co-precipitation, solution and incipient impregnation principle were used for Method 1 (M1), Method 2(M2) and Method 3 (M3) & Method 4 (M4) respectively. The performance of these catalysts was examined testing the activities that are expressed in terms of rate of reactions. In most cases, it is the intrinsic rate of the chemical reaction which is being sought because, mass and heat transfer effects brought about by gradients of concentration and temperature within the catalyst or the reactor give rise to apparent activities, which are virtually useless information. Therefore, it was decided to rank the prepared catalysts on the basis of intrinsic rate and stability.

Setting of the Experimental Conditions: The activity or rate determination experiments were carried out in a specially designed isothermal fixed bed stainless steel reactor having diameter of 3.00 cm (Fig. 3.5) and a catalyst bed height of 6-10 mm at atmospheric pressure and 200°C. Experimental conditions (Table 4.1) such as catalysts volume, space velocity, catalysts particle size, superficial velocity, pressure and inlet gas composition were set from the study of Begum (1992). On the other hand reduction time, reduction temperature and reaction temperature were selected through the experiments on the catalyst prepared by Method 3 (M3) and on the industrial catalyst. These experiments had two purposes; firstly, to set the experimental conditions for activity and stability study, secondly, to investigate the effect of the variables mentioned above on the activity of the prepared and industrial catalysts.

Table 4.1 Experimental Conditions for the Activity Testing of the Prepared and Industrial Low Temperature Shift Catalysts

Parameters	Reduction Conditions	Reaction Conditions
1. Temperature, °C	200	200
2. Pressure, atm	1	1
3. Volume of Catalyst, ml	3	3
4. Size of Catalyst, mesh	16-25	16-25
5. Space velocity at operating conditions, h^{-1}	25000 - 35000	35000 - 50000
6. Inlet Gas Composition (Dry Basis), mol %	Ar = 88-90	CO = 5-6
	H_2 = 12-10	Ar = 78-82
		H_2 = 14-15
7. Steam: CO ratio (molar)	-	12
8. Superficial Velocity, cm/s	4.75-4.8	8.6-9.3
9. Duration of experiment, hrs.	4	4 to 6

The results of the effect of reduction time and temperature are presented in Table 4.2. This study has revealed that reduction at 200°C for 4 hrs is adequate for both prepared and industrial catalysts. For constant reduction time of 3 hours, the prepared catalyst following M3 shows the same characteristic of industrial catalyst. In both the cases, the catalysts were best reduced at a temperature between 200 to 250°C. Hakkarainen and Salami (1989) found the similar results. In their study, a significant reduction of the catalyst and increase in the surface area were observed during the initial activation at 250°C. The rate of reaction is found significantly lower when the catalyst is reduced at a temperature of 300°C and 350°C. This is not unusual, since, at any temperature higher than 250°C, copper crystalline growth reduces surface area of the catalysts. The presence of steam, even in small amounts, in carrier gas can also cause crystalline growth. Since water is produced by the reduction reaction it is difficult to avoid it even with high purity hydrogen.

Table 4.2: Effect of Reduction Conditions on the Activity of the Catalyst Prepared By Method 3 and Industrial Catalyst, Composition of the Catalysts: CuO = 41%, ZnO = 31%

Exp. Run	Reduction Conditions		Catalyst Weight, gm		Conversion of CO, %		Rate × 1000 (g.mole CO converted/ (g.cat.hr.))	
	Temp , oC	Time (hrs.)	M3	Indus.	M3	Indus.	M3	Indus.
1	350	3	5.20	3.71	60.5	70.0	16.02	19.4
2	300		4.62	3.8	69.03	81.09	18.47	24.8
3	250		4.91	3.66	74.42	87.0	20.17	26.2
4	200		5.07	4.09	81.29	86.8	23.06	26.62
5	150		4.83	3.9	60.1	76.14	17.30	20.1
6	200	1	5.29	3.58	52.1	67.7	14.25	15.0
7		2	5.11	3.94	66.4	85.31	20.20	26.07
8		3	5.07	4.09	81.29	86.8	23.06	26.62
9		4	4.79	3.62	78.3	92.2	23.7	27.11
10		6	5.44	3.83	79.1	94.0	23.16	27.03

Reaction temperature is very important for catalyst life, especially for the catalysts having sintering tendency. This is why; the activity of the prepared catalyst was investigated using different reaction temperatures. The results of the effect of reaction temperature on the catalyst prepared by M3 are given in Table 4.3. It is observed that the rate of reaction increases with the increase of temperature up to 300°C and at 400°C rate decreases significantly due to sintering of the catalysts particle at elevated temperature. Sintering is primarily a thermal process of pore collapse and crystallite growth, although chemical interactions with reactants may also play secondary roles. The consequences of pore collapse in the support are twofold. First, crystallites of active components are encapsulated in the smallest pores and become inaccessible. Second, the dispersing function of the support is diminished. Supported crystallites move closer together, accelerating loss of the active surface area. In this thesis work, zinc is used as promoter, which prevent collisions between migrating crystallites in some extent and also restrict intercrystallite transport acting as preferential adsorbents. High surface area zinc oxide used in industrial catalysts, also adsorbs chlorine, further protecting the copper crystallites. Use of zinc probably prevents the catalysts from sintering up to 300°C.

Table 4.3 Effect of Reaction Temperature on the Activity of the Prepared Catalyst by M-3 and the Industrial Catalyst, Composition of Catalysts: CuO = 41 % and ZnO = 31%

Exp. Run	Reaction Temperature, °C	Conversion of CO, %		Rate × 1000 (g.mole CO converted/ (g.cat.hr.))	
		M3	Indus.	M3	Indus.
1	150	68.7	78.4	18.23	22.7
2	200	74.7	86.9	21.82	25.24
3	250	73.5	91.12	21.15	26.9
4	300	78.6	92.3	25.6	28.12
5	350	77.5	90.1	26.01	26.03
6	400	61.9	70.5	17.5	20.25
Weight of Catalyst (gm)		4.2612	3.9172	4.2612	3.9172

The results of the activity testing are presented in Figures 4.1, 4.2, 4.3, 4.4 and 4.5. Calculated data are presented in the tables of Appendix D. Relative performance of the laboratory scale preparation methods compared to industrial method are presented in Fig.4.1 which shows that the catalysts prepared by co-precipitation and incipient impregnation method have higher activity than the catalyst prepared by solution technique. It is worth mentioning that catalyst of same composition (CuO = 41% and ZnO = 31%) prepared by co-precipitation method (M1) has higher activity than the activity of catalysts prepared by impregnation method. This is, probably, because of non-uniform structure of γ-Al_2O_3 used in impregnation methods (M3 and M4). Both M3 and M4 methods were closed to industrial catalyst preparation method. But, M3 seems better than the other impregnation method-M4. That is why M3 captures out interest for further study. The catalyst prepared by this method was used for Temperature Programmed Reduction (TPR), short-term and long-term stability study. It is significant that industrial catalyst, prepared by impregnation method, has higher activity than the laboratory scale prepared catalysts.

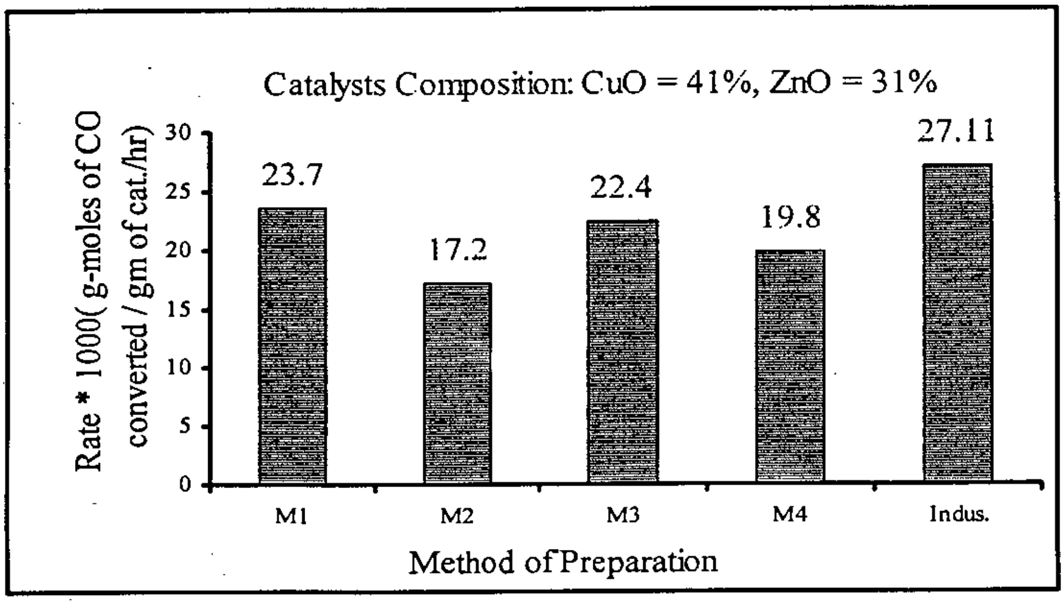

Fig. 4.1: Laboratory Scale Catalyst Preparation Methods and Their Comparison with Commercial Method

Perhaps, this is because of dispersion of the active component Cu. In industrial catalyst, percentage of active component available on the surface was higher than the availability of the active component on the surface of the prepared catalysts because in the prepared catalysts the active component is dispersed throughout the body of the catalyst pellets, especially in the case of catalyst prepared by co-precipitation and solution technique (Table 4.5).

To check the influence of composition on the activity of the catalysts, samples were prepared using different composition following M1, M2, M3 and M4. In every case, the results were compared with the activity of industrial catalyst. The results of the activity testing of these samples are presented using bar charts in the Figures 4.2, 4.3, 4.4, and 4.5. In all cases, it is observed that the conversion of CO changes significantly if the concentration of CuO in the catalyst samples changes from 15 to 35%. But, no considerable difference in rate has been noticed at higher CuO loading (35-41%). In the case of M1, the sample containing 35% CuO has higher activity than that of the sample containing 41% (Fig.4.2). In the case of M2, M3 and M4, the activity of the samples having 35% CuO are also close to the activity of the samples containing 41% CuO. Campbell (1970) pointed out that copper is the active species for the LTS reaction and initial activity is proportional to copper content. The activity testing results of this work shows the same trend.

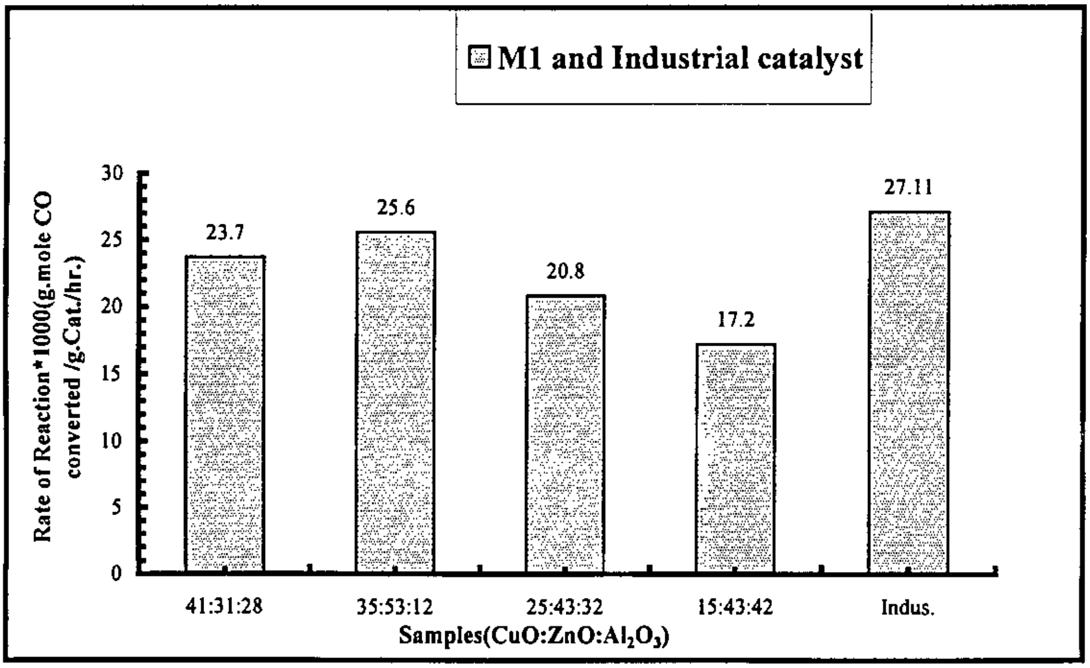

Fig. 4.2: Effect of Composition on the Activity of the Prepared Catalyst Following Method 1 (M1)

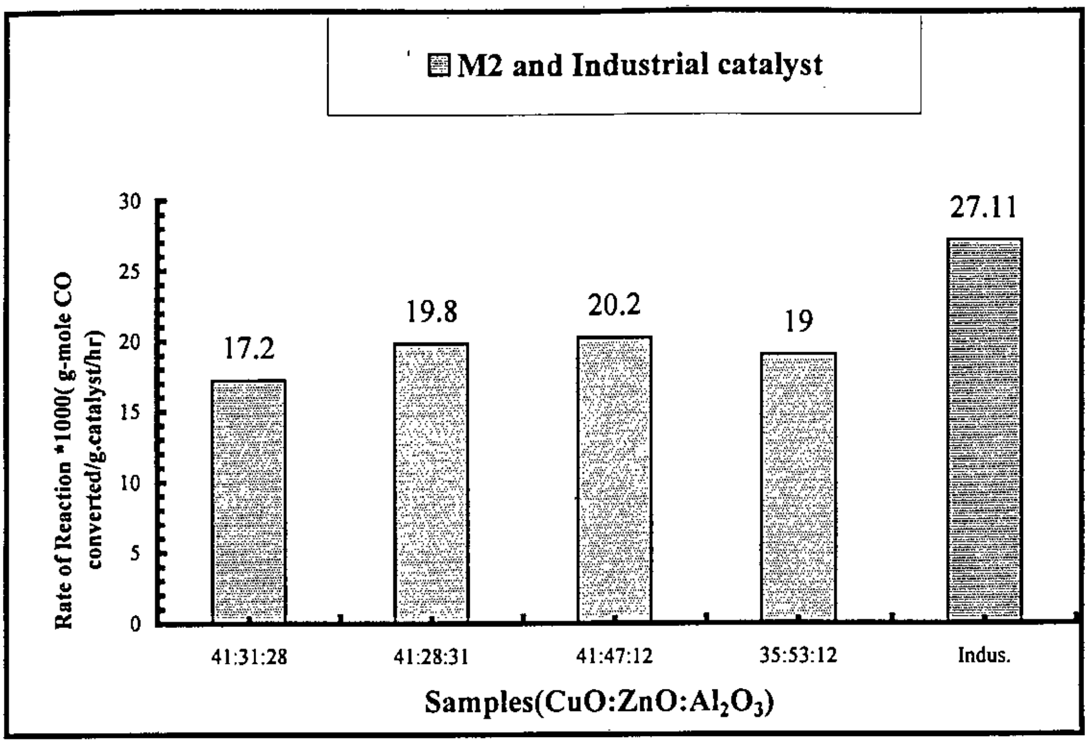

Fig. 4.3 Effect of Composition on the Activity of the Prepared Catalyst Following Method 2(M2)

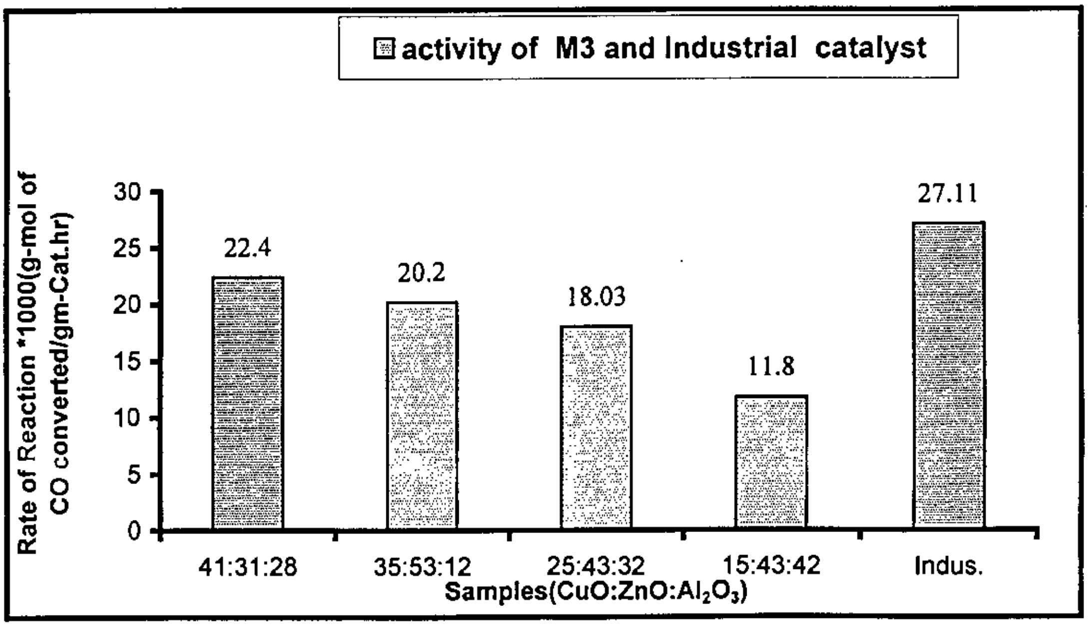

Fig. 4.4 Effect of Composition on the Activity of the Prepared Catalyst Following Method 3 (M3)

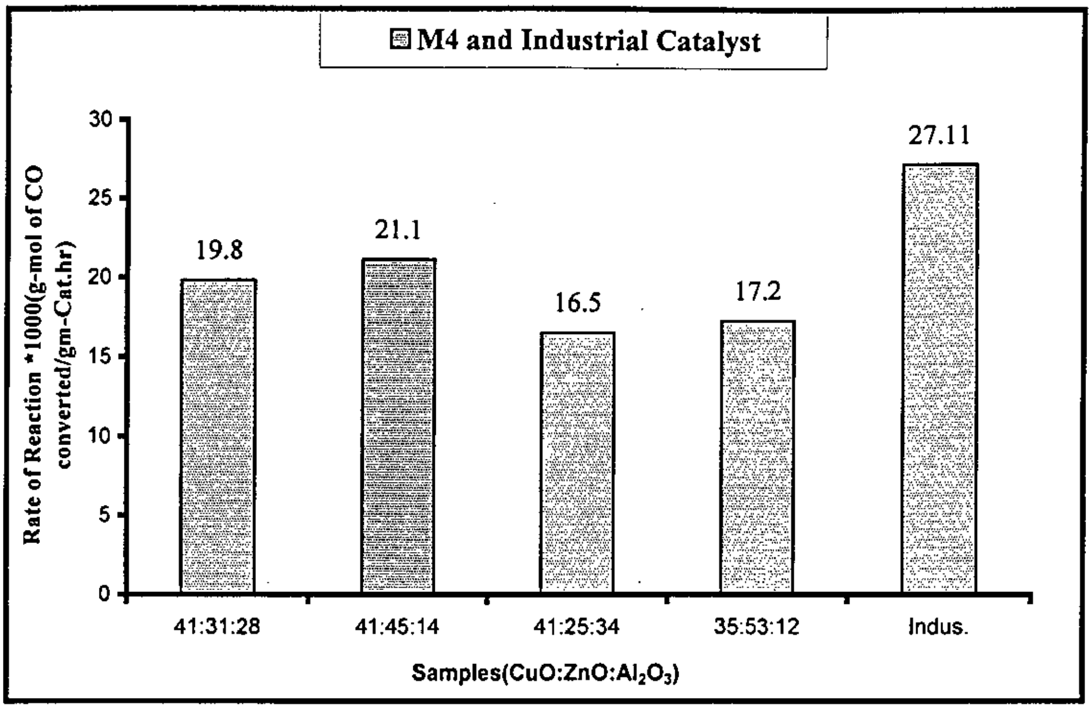

Fig. 4.5 Effect of Composition on the Activity of the Prepared Catalyst Following Method 4 (M4)

In impregnation methods (M3 and M4), γ-Al_2O_3 is used on which the active component and promoter are impregnated. The procedures of the catalyst preparation have been discussed elaborately in chapter 3 (Section3.1). As per the preparation procedure, there is a significant difference between M3 and M4. In M3, γ-Al_2O_3 particles were suspended for a particular period; on the other hand in M4 particles were mixed and calcined thereafter. In the case of M3, the pores of the support particles were sufficiently loaded with active metal salt solution. One thing should be noted here that drying was not performed for the catalyst prepared by M4 but drying is very important to crystallize the salt on the pore surface. If drying is not performed properly, irregular and uneven concentration distribution can result. If drying rate is too slow, evaporation occurs at the miniscus, which retreats down the pore and solute concentrates deeper in the pore. When finally crystallized, the salt is located at the bottom of a pore or at the particle center. When the drying rate is too fast, a temperature gradient occurs. Vaporization deep in the pore forces solution toward the outside, where most of the deposition takes place consequently non-uniform deposition forms over the surface. In the case of M3, drying actually occurs during calcination. As the slurry is suddenly exposed to high temperature, evaporation rate becomes very high which causes the non-uniform deposition of active component. This is the main reason to get the pore activity of the catalyst prepared by M4 relative to the catalyst prepared by M3. Reviewing the Fig.4.4, it can be noted here that at higher concentration of CuO, the catalyst prepared by M3 has very good activity and is compatible with the industrial catalyst. So, M3 can be a potential preparation method for commercial purpose and it deserves further study.

Data presented in the Table 4.4 shows the results of the effect of ZnO/Al_2O_3 ratio on the activity of catalysts prepared by Method 2 and Method 4. For the same method of preparation and same concentration of the active component the activity of the prepared catalysts increases with the increase of ZnO and Al_2O_3 ratio. These results reveal that the promoter (ZnO) has an important role on activity of the prepared catalysts.

Table 4.4 Effect of ZnO and Al_2O_3 Ratio on the Activity of the Prepared Low Temperature Shift Catalyst; Experimental Conditions are given in Table 4.1

No. Obs.	Method of Prep.	Catalyst Compositions			$\frac{ZnO}{Al_2O_3}$ (wt ratio)	Rate × 1000 (g.mole CO converted/ (g.cat.hr.))
		CuO	ZnO	Al_2O_3		
1	M2	41	31	28	1.11	17.2
2	M2	41	28	31	0.90	19.8
3	M2	41	47	11	4.27	20.2
4	M4	41	31	28	1.11	19.8
5	M4	41	45	14	3.21	21.1
6	M4	41	25	34	0.73	16.5

4.2 STABILITY STUDY OF THE PREPARED AND INDUSTRIAL LTS CATALYSTS

It is well known that long-term activity testing can assess the aging of catalysts. In this research work, catalyst prepared by M1 & M3 and industrial catalyst are assessed by both short-term and long-term activity testing at different experimental conditions. The results of this study are discussed in this section. The short-term stability test results of the prepared and industrial catalysts are shown in Fig. 4.6 using rate of reaction vs. time curve. Duration of this experiment was 12 days. But, it should be noted here that the experiments were not conducted continuously.

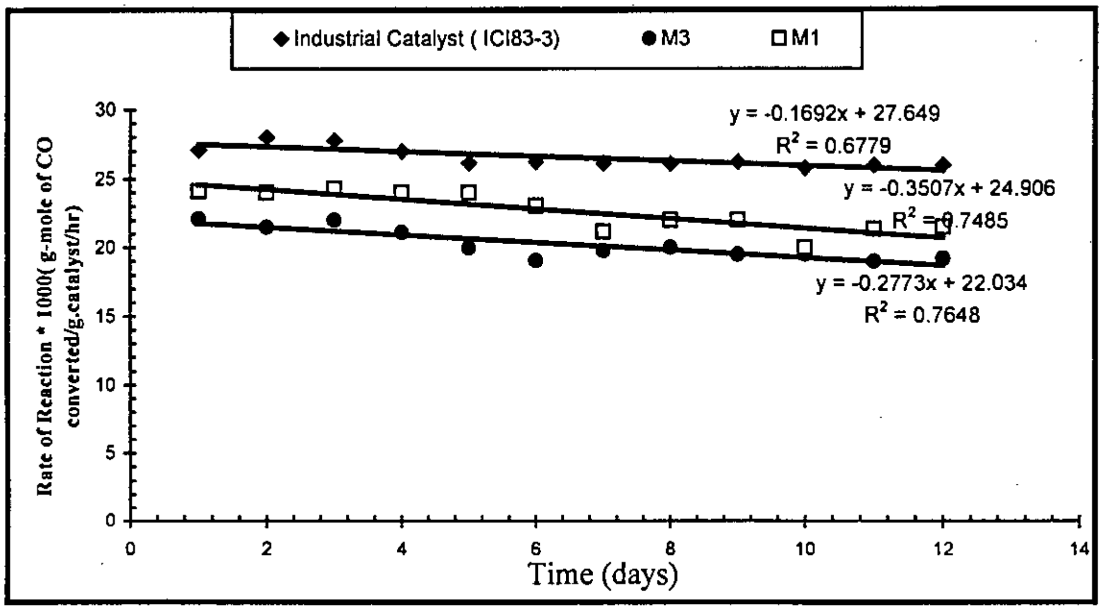

Fig. 4.6 Comparison of Short-term Stability Study of the Prepared (M1 and M3) and Industrial Catalysts, Catalyst Composition: CuO = 41%, ZnO = 31%, Catalysts Size: 16-25 Mesh

These experiments were conducted for five days in a week and the experimental conditions were same as the conditions mentioned in the Table 4.1. Observing the slopes of the best fitted straight lines, it can be concluded that industrial catalyst was more stable than the prepared catalysts. Specially, the catalyst prepared by M1 is less stable than the catalyst prepared by M3 and the industrial catalyst. In the short-term and heat transfer limitations. Again, small size catalyst particles are prone to sintering at elevated temperature. So, short-term activity testing is not enough to be confirmed about the life of the catalysts. This is why the long-term stability testing was performed.

The catalysts prepared by M3 and industrial catalyst were used for long-term stability study and the tests were performed for 12 and 6 weeks respectively. In this case, the catalysts size was different than the size of the catalysts used in short-term stability study. Space velocity was about 9500 h^{-1} in average. Actually, the conditions selected for the long-term stability study were close to industrial reaction conditions. During this study, the catalysts were reduced everyday before starting the reaction for activity testing. After testing, the reaction gas mixture was replaced by Ar-H_2 gas mixture. The catalyst bed was then purged for 30 to 45 minutes at 200°C. Then the reactor heater was disconnected from power source and the reactor was kept under Ar-H_2 mixture till next morning at 20 to 30 psig and room temperature. The results of long-term stability test are shown in Figure 4.7. The linear best fitted trend line for industrial catalyst is extended

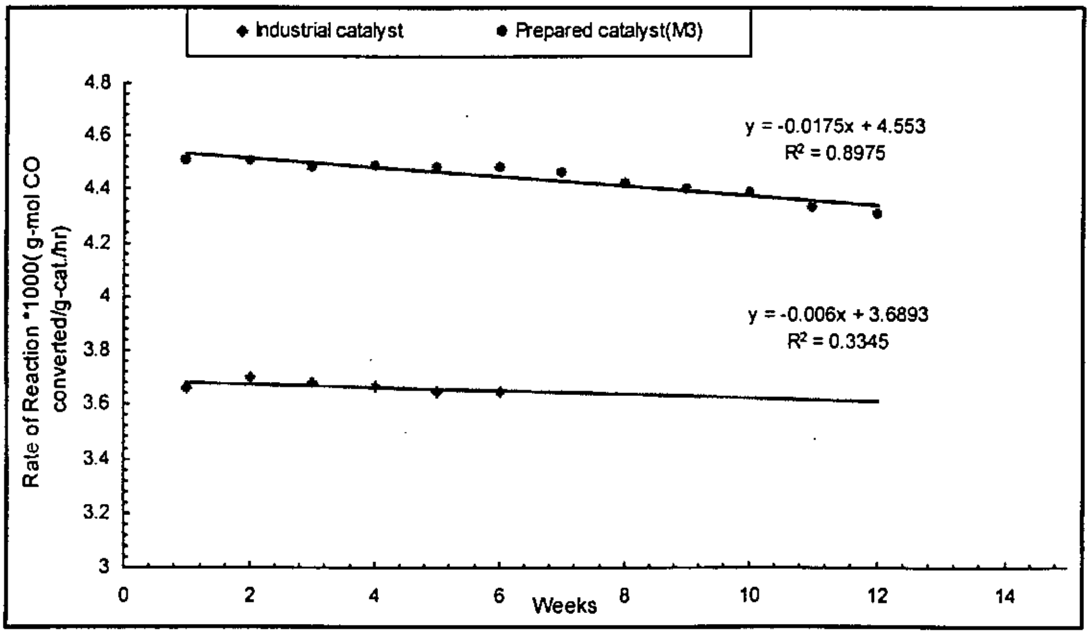

Fig. 4.7: Long-Term Stability Study of the Prepared (M3) and Industrial Catalysts, Composition of Catalysts: CuO = 41%, ZnO = 31%, Catalysts Size: 4-6 mesh, Formulation Pressure of Prepared catalyst: 400 kg/cm^2

up to 12th week to compare the result with prepared catalyst. Experimental conditions for long-term experiment are given below:

Reduction Conditions for Prepared Catalyst (M3):

1) Feed gas compositions, mole %: $H_2 = 38$ and $N_2 = 62$
2) Space velocity, hr^{-1}: 1600
3) Temperature: 200°C
4) Duration: 3 hrs.

Reduction Conditions for Industrial Catalysts:

1) Feed gas compositions, mole %: $H_2 = 45$ and $Ar = 55$
2) Space velocity, hr^{-1} : 2500
3) Temperature: 200°C
4) Duration: 3 hrs.

Reaction Conditions for the Prepared (M3) and Industrial Catalyst:

1) Feed Compositions, mole %: $H_2 = 62$, $N_2 = 30$ and $CO = 8$
2) Space Velocity (hr^{-1}): 9300-9600
3) Temperature: 200°C
4) Duration: 4-5 hrs.

From the straight lines (Fig. 4.7) of the rate of reaction vs. time (week) curve, it is observed that the rate of reaction of the prepared and industrial catalyst will be zero after 260 and 614 weeks respectively. From this observation, it is clear that under studied condition industrial catalyst is much more stable than the prepared catalyst by M3. Industrial catalysts use additives to improve stability improving the physical properties. In the case of industrial catalyst, robustness of the pellets has considerable practical importance. Soft pellet may have a higher initial activity due to being less firmly compressed but more likely to break up in service and lead to a premature catalyst change. The Method 3 can be a potential method for pilot plant or industrial catalyst preparation method if Mn, Ce and Fe can be used with Cu to enhance the stability. Flytzani-Stephanopoulous et al. (2001) studied that addition of

Fe and Ce significantly improves the stability of LTS catalyst. Jovanovic, et al. (1988) also studied that small addition of small amount of Mn not only increase the activity but also increase the stability of LTS catalyst.

From the long-term stability study it is observed that the activity of laboratory scale prepared catalyst is higher than that of the industrial catalyst, although, in the case of short-term stability the activity of the laboratory scale prepared catalysts is lower. This is probably due to experimental conditions and formulation variables of the catalysts. In the short-term stability testing catalyst size was 16-25 mesh and space velocity was 33000 to 50000 h^{-1}. Mass transfer limitations were relatively lower in the case of short-term stability test due to smaller size particles both for the laboratory scale prepared and industrial catalysts. So, rate of reaction was completely dependent on the accessible active metal area. As the active metal area of industrial catalyst (3.01 m^2/gm) is higher than that of laboratory prepared catalysts (Table 4.5), the rate is also higher. On the other hand, in the long-term stability testing catalyst size was 4-6 mesh and space velocity was 9500 h^{-1} on average. So, both external and internal molecular diffusion were important factors. The laboratory scale catalyst pellets (4-6mesh size) were prepared at a pressure of 400 kg/cm^2 that causes the catalyst particles loosely bound. For this reason, reactant molecules get easy access to the interior active surface area, that means laboratory scale catalyst has less mass transfer diffusion problem than that of the industrial catalyst. The result of long-term stability testing also represents this interpretation.

4.3 CHARACTERIZATION OF THE SELECTED PREPARED AND INDUSTRIAL CATALYST

BET surface area, total pore volume and active metal surface area were determined to characterize the catalysts prepared by different laboratory scale preparation methods and the industrial catalyst. The physical characterization results are presented in Table 4.5 and in Figures 4.8 to 4.12. BET surface area, total pore volume and active metal surface area were determined using the Pulse ChemiSorb

2705. The active metal surface areas of the catalysts were determined by H_2 chemisorption. The experimental conditions are given in Table D.8 of Appendix D. Results in Table 4.5 show that the industrial catalyst has significantly higher active metal surface area. The BET surface area and metallic dispersion data are found in agreement with the activity testing results provided the reaction conditions and catalyst composition remain unchanged. It is noticeable that both the BET surface area and the total pore volume of the prepared catalyst following M1 is higher than that of the industrial catalyst, but the active metal surface area of industrial catalyst is significantly higher than the other prepared catalysts. This is probably because of the difference in crystal structure between the laboratory scale catalysts and industrial catalyst. It is known that active metal surface area increases with the increase of small stable crystallite. But, BET surface area and total pore volume do not depend on it.

Table 4.5: Characterization of Laboratory and Industrial Catalyst. Composition of the catalysts: CuO = 41 % and ZnO = 31 % and Al_2O_3 = 28 %, Catalysts Particle Mesh Size: 30-34

Method Of Preparation	Bet Surface Area (m^2/gm)	Active Metal Surface Area (m^2/gm)	Total Pore Volume(95-98 % Saturation) (mm^3/gm)
M1	50.36	1.78	52.12
M2	28.29	1.26	33.40
M3	39.65	1.68	43.62
M4	34.23	1.42	35.30
Indus.	46.20	3.01	47.13

Figures 4.8 and 4.9 show the Temperature Programmed Reduction (TPR) profiles of the prepared catalyst (M3) and the industrial catalyst respectively. Figures 4.10, 4.11 4.12 are the TPR profiles of pure CuO, ZnO and Al_2O_3 respectively. The experimental conditions and procedure for TPR experiment are described in chapter 3 (Section 3.3.3).

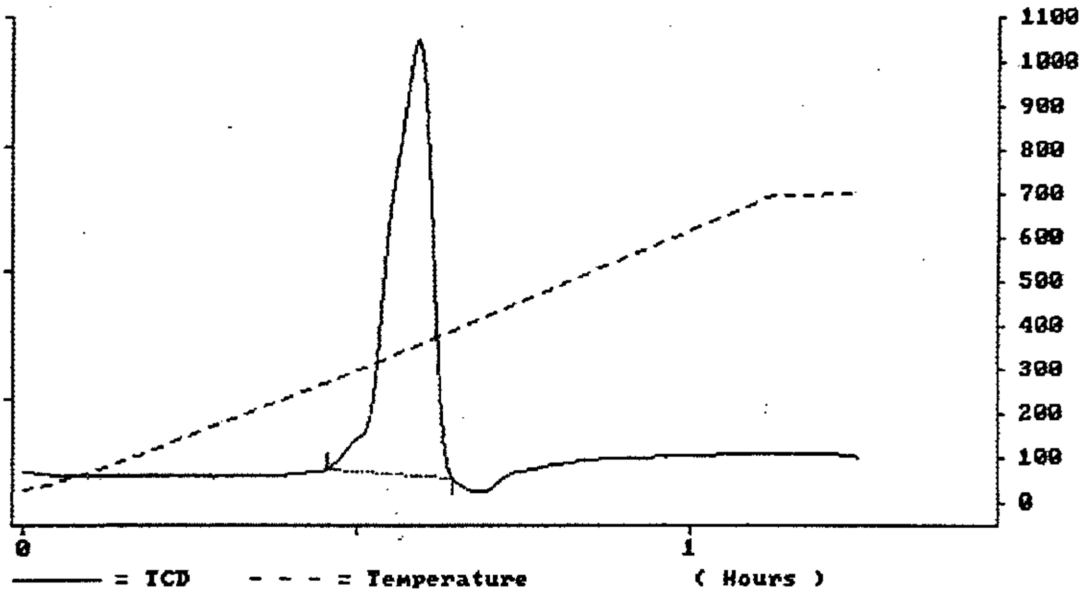

Fig. 4.8 Temperature Programmed Reduction (TPR) of the Prepared Catalyst (Method 3)

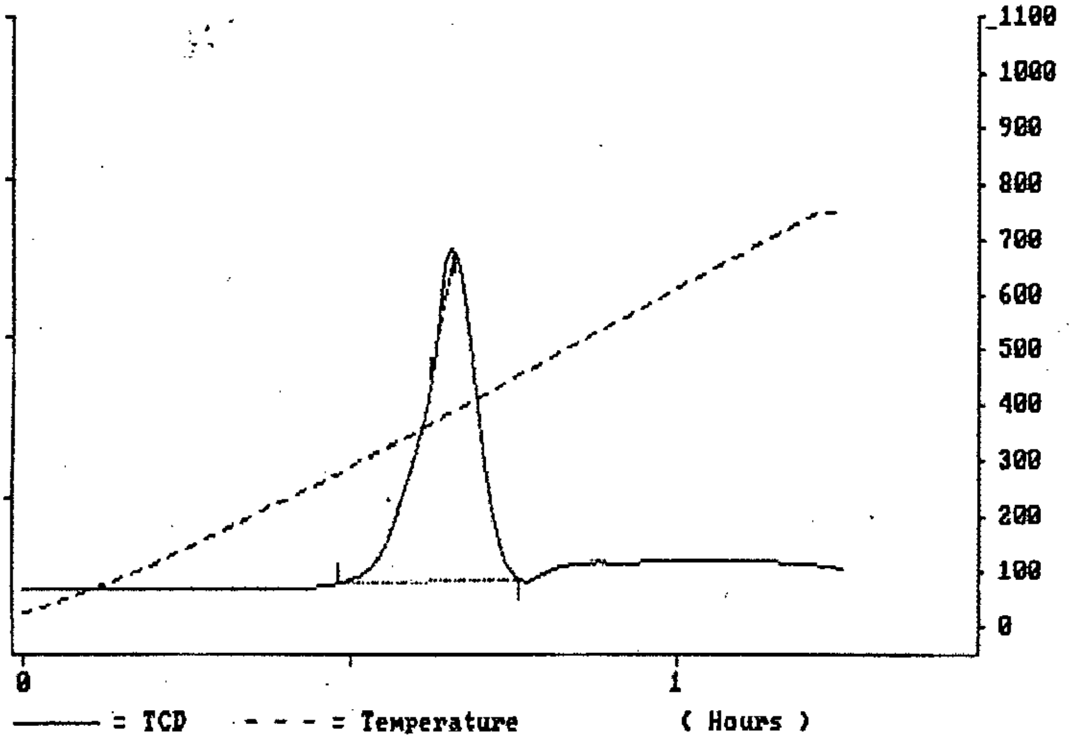

Fig. 4.9 Temperature Programmed Reduction (TPR) of the industrial Catalyst

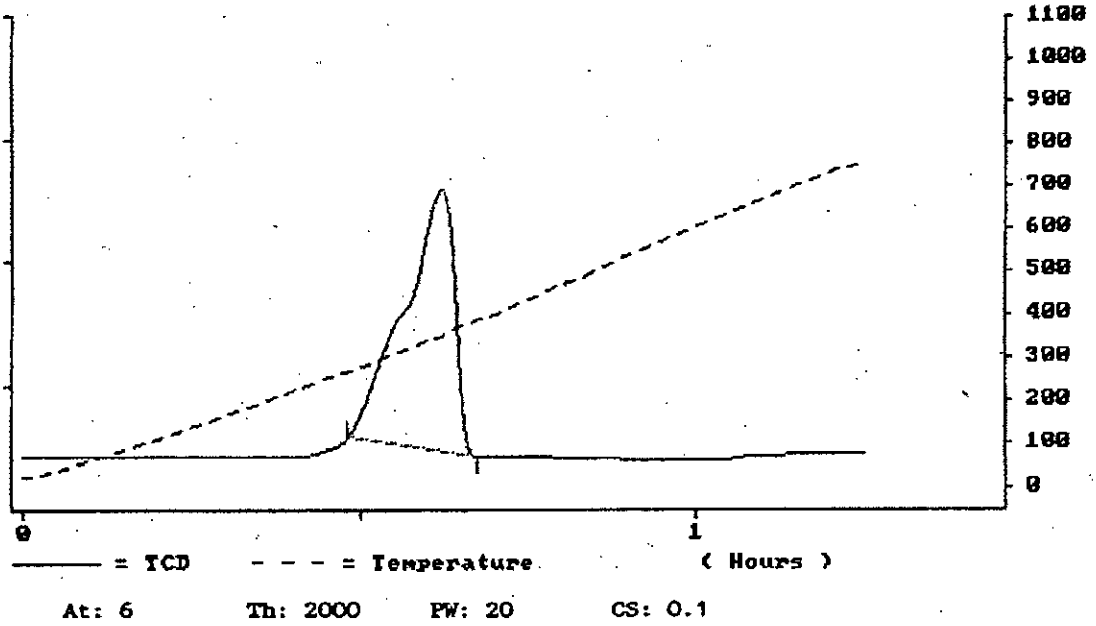

Fig. 4.10 Temperature Programmed Reduction (TPR) Profile of CuO

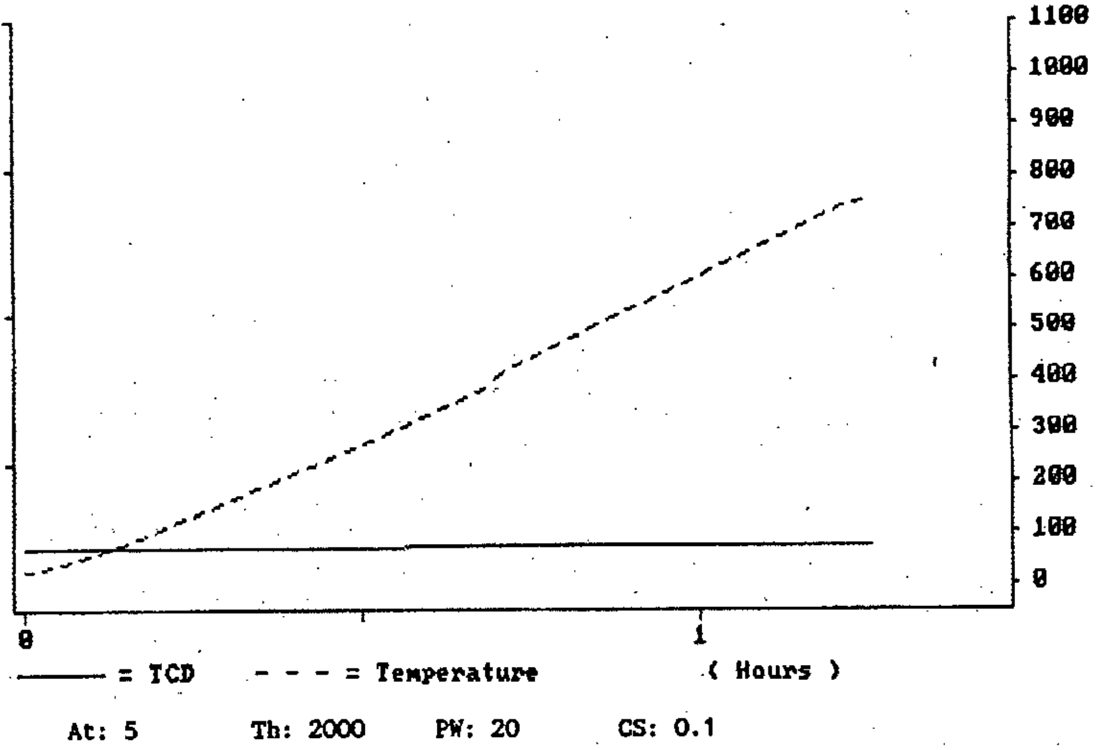

Fig. 4.11 Temperature Programmed Reduction (TPR) Profile of ZnO

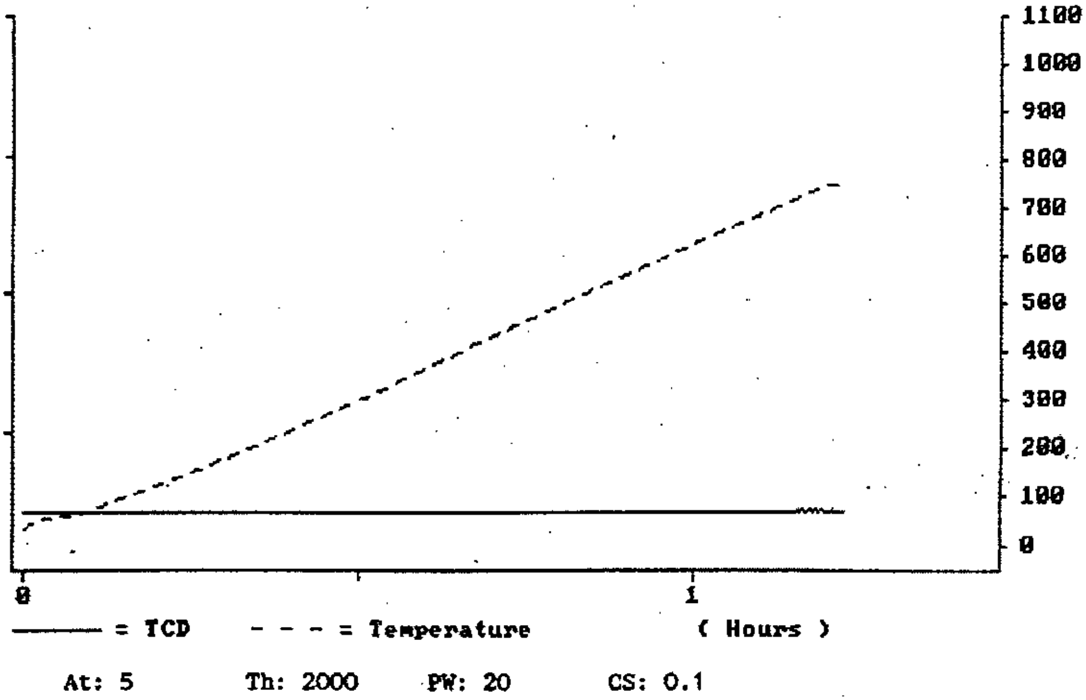

Fig. 4.12 Temperature Programmed Reduction (TPR) Profile of Al_2O_3

From the Fig.4.11 and 4.12, it is clear that there is no peak of ZnO and Al_2O_3 available before 750°C. The reduction time and temperature of the pure CuO are found to be 37:15mins and 348°C respectively (Fig.4.10). Examining the peaks of the Figures 4.8 and 4.9, reduction time and temperature are found to be 35:27 mins and 355°C respectively for the prepared catalyst, 39:15min and 386°C for the industrial catalyst. The reduction temperature values of the catalysts are close to the reduction time of the pure CuO. So, it is obvious that the peaks of the Fig.4.8 and 4.9 are of CuO. Comparing the Fig.4.8 and 4.9, it can be mentioned here that some CuO molecule of the industrial catalyst are close to the formation of complex with other components, for which reason the position of the peak has shifted towards the right and the reduction temperature become higher.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

This study has been carried out to investigate the effects of the different catalyst preparation methods on the activity and stability and to find out an effective method for catalyst preparation. Laboratory scale catalysts have been prepared using co-precipitation, solution and incipient wet impregnation techniques. Catalyst prepared using impregnation principle (Method 3) has been used for stability study. The activity and stability study of the commercial and the prepared catalysts have been conducted in a stainless steel fixed bed reactor. Catalysts are characterized using Pulse ChemiSorb 2705 of Micromeritics, USA.

From the experimental data and subsequent analysis, the following conclusions may be drawn:

1. The preparation method, preparation variables and operating conditions have significant influence on the activity of the LTS catalyst. Catalyst prepared by impregnation principle (Method 3) is proved to be effective among other catalysts.

2. The composition of the catalyst has got strong influence on the activity. With the increase of copper loading and ZnO/Al_2O_3 ratio, the activity of LTS catalyst increases considerably.

3. It is found that the catalyst prepared following Method 3 (M3) and the industrial catalysts have got same optimum reduction and reaction temperature.

4. The result of the long-term activity study has revealed that the prepared catalyst following M3 is less stable than industrial catalyst but M3 can be considered as a promising catalyst preparation method.

5. From the Temperature Programmed Reduction (TPR) result, it is found that CuO in industrial catalyst has a tendency to form complex with other components.

Various constraints of the experiment and lack of facilities prevented the investigation from being complete. The following actions should be undertaken in future to improve the accuracy of the catalyst study.

1. The short-term and long-term stability tests could be run continuously rather than 4-6 hours a day and 5 days a week because thermal thrust affects the crystal structure and catalyst life thereof.
2. Catalysts could be made using additives such as Fe, Mn, Ce and colloidal silica to enhance the stability.
3. The effect of reactant gas composition, calcination conditions on the activity of catalyst could be studied.
4. Effect of γ-Al_2O_3 particle size on the activity of the catalyst prepared following M3 could be examined. α- Al_2O_3 could be used instead of γ-Al_2O_3 during catalyst preparation in future.

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APPENDICES

APPENDIX A

Chemical and Physical Properties Data and Figures

Table A.1: Calculated Values of Equilibrium Constants of Shift Reaction in the Temperature Range of 226 to 627°C

T (K)	t(oC)	K[Gupta et al.,1981]	K[Rechardson et al.,1989]
500.0	226.8	136.1	126.0
550.0	276.8	57.5	-
573.2	300.0	42.9	-
600.0	326.8	28.1	27.08
650.0	376.8	15.5	-
673.2	400.0	12.6	-
700.0	426.8	9.34	9.017
750.0	476.8	6.05	-
773.2	500.0	4.90	-
800.0	526.8	4.185	4.038
850.0	576.8	3.028	-
873.2	600.0	2.430	-
900.0	626.8	2.280	2.204

Table A.2 Free Energies and Heat of Reaction for Water-Gas Shift Reaction

Temperature (K)	Free Energy (Cal/mol)	Heat Effect (Cal/mol)
0	-9662	-9662
298	-6817	-9838
300	-6799	-9837
400	-5802	-9710
500	-4850	-9520
600	-3933	-9294
700	-3059	-9051
800	-2219	-8802
900	-1413	-8552
1000	-631	-8311

Table A.3: Saturated Vapor Pressure of Water

T is in ^{o}C
P is in mm (Hg)

T	P	T	P	T	P	T	P	T	P	T	P
-10	2.1	11	9.8	32	35.7	53	107.2	74	277.2	95	633.9
-9	2.3	12	10.5	33	37.7	54	112.5	75	289.1	96	657.6
-8	2.5	13	11.2	34	39.9	55	118.0	76	301.4	97	682.1
-7	2.7	14	12.0	35	42.2	56	123.8	77	314.1	98	707.3
-6	2.9	15	12.8	36	44.6	57	129.8	78	327.3	99	733.2
-5	3.2	16	13.6	37	47.1	58	136.1	79	341.0	100	760.0
-4	3.4	17	14.5	38	49.7	59	142.6	80	355.1		
-3	3.7	18	15.5	39	52.4	60	149.4	81	369.7	102	815.9
-2	4.0	19	16.5	40	55.3	61	156.4	82	384.9		
-1	4.3	20	17.5	41	58.3	62	163.8	83	400.6	104	875.1
0	4.6	21	18.7	42	61.5	63	171.4	84	416.8		
1	4.9	22	19.8	43	64.8	64	179.3	85	433.6	106	937.9
2	5.3	23	21.1	44	68.3	65	187.5	86	450.9		
3	5.7	24	22.4	45	71.9	66	196.1	87	468.7	108	1004
4	6.1	25	23.8	46	75.7	67	205.0	88	487.1		
5	6.5	26	25.2	47	79.6	68	214.2	89	506.1	110	1075
6	7.0	27	26.7	48	83.7	69	223.7	90	525.8		
7	7.5	28	28.3	49	88.0	70	233.7	91	546.1	112	1149
8	8.0	29	30.0	50	92.5	71	243.9	92	567.0		

Table A.4 Specification of the Chemicals Used for the Experiments

No.	Name	Chemical Formula	Name of the manufacturer	Chemical analysis of the reagent
1.	Copper (II) nitrate-3-hydrate	$Cu(NO_3)_2.3H_2O$	Riedel-de haen	$Cu(NO_3)_2.3H_2O$ = 99%; Fe = 0.01%, Cl = 0.005%, SO_4 = 0.01%
2.	Zinc nitrate-6-hydrate	$Zn(NO_3)_2.6H_2O$	E. Merck (India)ltd.	$Zn(NO_3)_2.6H_2O$ = 96%, HNO3 = 0.05%, Cl = 0.005%, SO_4 = 0.01%, Heavy metals = 0.002%, Iron (Fe) = 0.001%
3.	Aluminum nitrate-9-hydrate	$Al(NO_3)_2.9H_2O$	E. Merck (India)ltd.	$Al(NO_3)_2.9H_2O$ = 95%, Cl = 0.005%, SO_4 = 0.03%, Heavy metals = 0.005%(as Pb), Iron (Fe) = 0.01%
4.	Alumina	Al_2O_3	Norton-hydronyl	Particle size = 16-32 mesh Surface area =235 m^2/gm
5.	Potassium hydroxide pellets	KOH	E. Merck (Germany)	KOH> 85%, k_2CO_3<2%, Cl<0.004%, PO_4<0.002%, Fe< 0.001%, Al<0.001%, Zn<0.0025%, As<0.0003%, Pb<0.0005%, N<0.0005%, SO_4< 0.003%, SiO_2 <0.01%, Ca <0.002%
6.	Zinc oxide	ZnO	E. Merck (India)Ltd.	ZnO = 99%, Cl = 0.02%, SO4 = 0.01% water soluble substances = 0.3%, Heavy metals = 0.01%

Table A.5 Specification of Industrial Catalyst (ICI Katalco 83-3)

Physical Properties	
Form	Pellets
Diameter	5.2 mm
Length	3.0 mm
Bulk Density	1,380 kg/m^3
Crush Strength:(axial)	220 kgf
Chemical Compositions	
CuO	41%
ZnO	31%
Al_2O_3	Balance

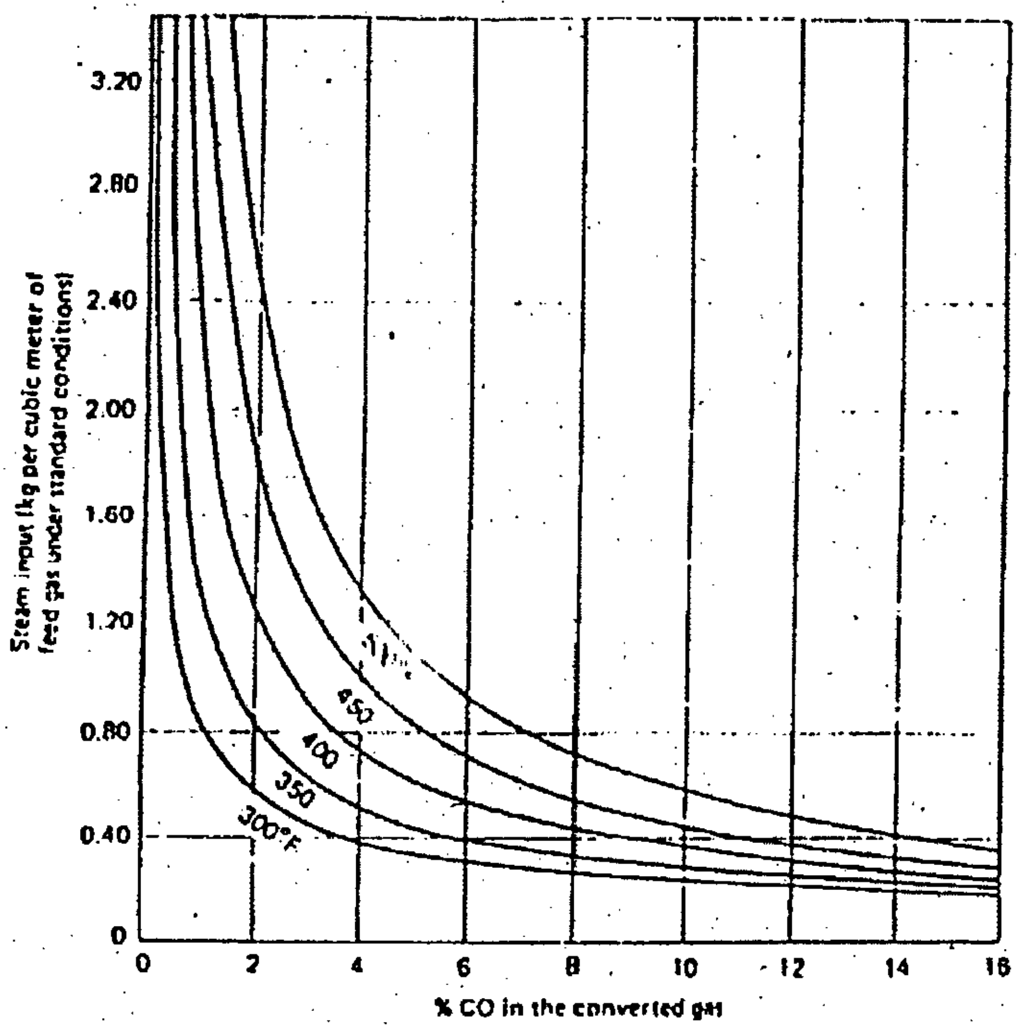

Fig.A.1: Steam Required at Achieved CO Conversion At Different Temperature In A Single-Stage Water-Gas Shift Reactor (Based On Data By Fauser).

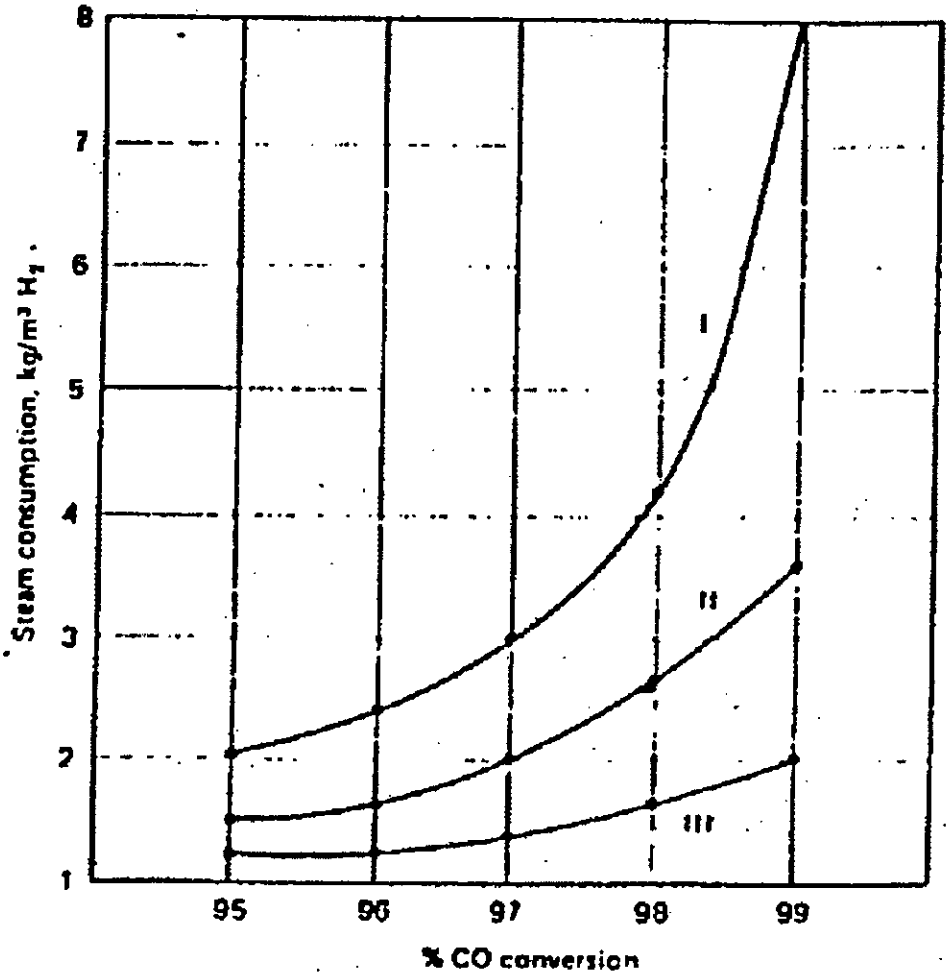

Fig.A.2: Steam Consumption During CO Conversion ((I) single-stage conversion, (II) two-stage conversion with equal change of heat between both stages, and (III) two-stage conversion with equal degrees of conversion (Based on data by Nitschmann)).

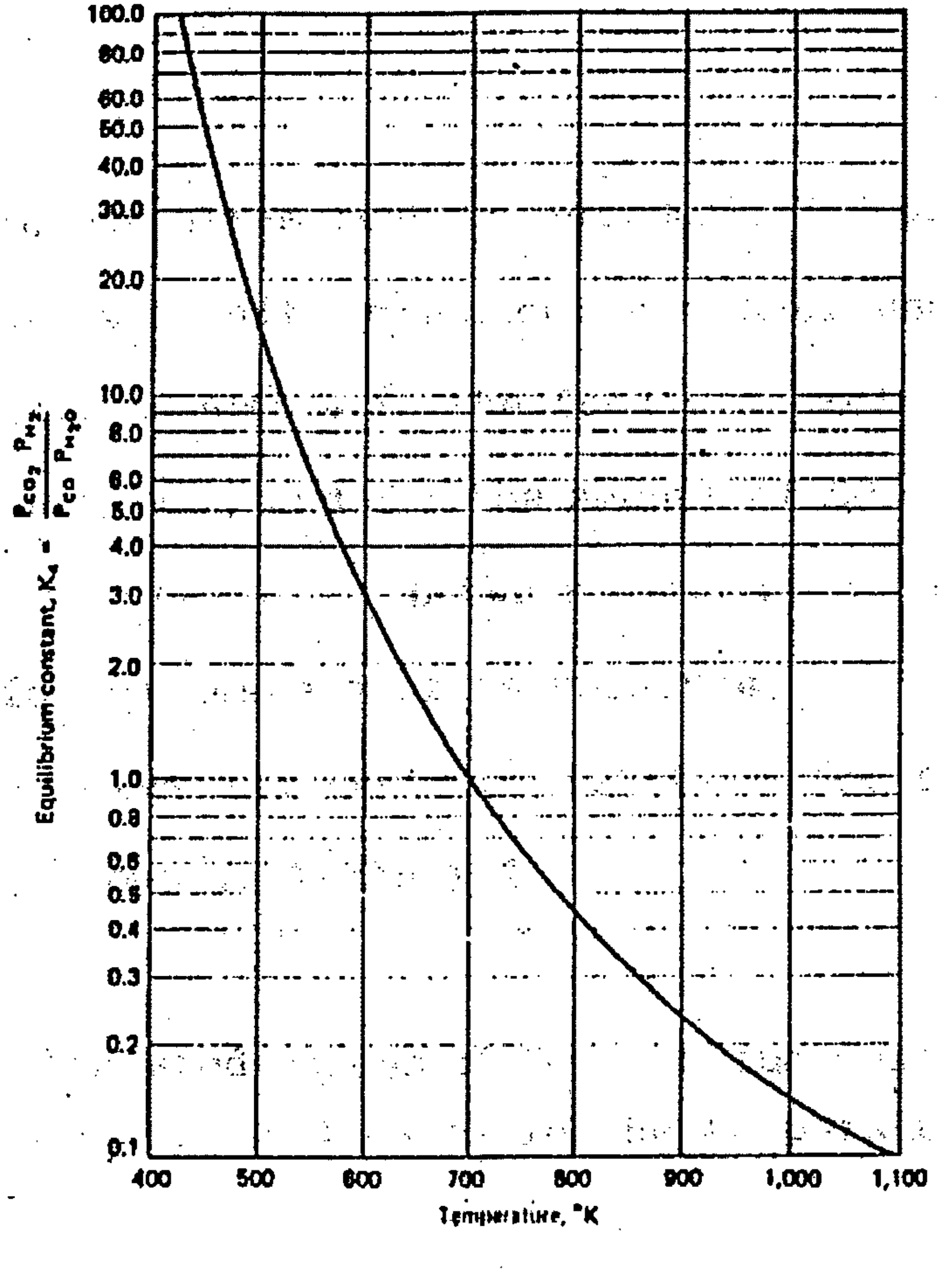

Fig.A.3: Effect of Temperature on the Equilibrium Constant for the Water-Gas Shift Reaction at 1 atm.

APPENDIX B

Observed Data Sheet

Test: Stability Test of Prepared Catalyst by Method 1, Run 1, Table D.1

Date of Experiment: 24.02.04

Name of the catalyst: Prepared by M1	**Comments (if any):**
Volume of Catalyst (ml): 3	
Weight of Catalyst (gm): 3.70	
Mesh Size: 16-25	

Reduction conditions:

Start at: 8:30 AM	End at: 11:30 AM	Flow rate of Ar(L/hr):25
Temperature (°C): 200		Flow rate of H_2(L/hr):10
Pressure (atm): 1		Flow rate of CO(L/hr):5
Duration (hrs): 3		

Reaction Conditions:

Start at: 11:30 am	End at: 4:30 pm	Flow rate of Ar (L/hr): 25
Temperature (°C): 200		Flow rate of H_2 (L/hr): 10
Pressure (atm): 1		Flow rate of CO (L/hr): 5
Duration (hrs): 4hrs. 30 mins.		Water rate (ml/h): 44ml/hr.

Sample Collection and Analysis:

GC analysis:							
Sample Gas Run							
Column: Molecular Sieve				Column: Porapak			
Report No: 1286				Report No.: 1291			
R.T	Peak Area	Comp.	%mol	R.T	Peak Area	Comp.	%mol
0.908	781	-		1.312	1383114	-	
1.01	2178	H_2		2.652	199358	CO_2	
1.43	1311020	Ar					
5.2113	30756	CO					
Standard Gas Run							
Report No.: 1281				**Report No: 1292**			
0.575	630	-	-	0.138	4082	N_2	
1.02	2329	H_2	48.27	1.313	134133	CH_4	
1.577	105073	Ar	5.43	1.557	1279268	CO_2	1.4
2.165	549789	N_2	31.8	2.728	28021	C_2H_6	
3.797	129072	CH_4	8.37	3.233	1551		
5.133	109169	CO	6.13	4.067	309		
Wet Test Meter Reading, Time for 1 dm^3 flow: 130 sec.							
Room Temperature (°C): 27.5							
Wet Test Meter Temperature (°C): 27							

APPENDIX C

Sample Calculation

Stability Test of Prepared Catalyst by Method 1, Run 1, Table D.1

1. Basic experimental data
   a) Inlet components: N_2, H_2, CO and steam
   b) Wet test meter temperature: 26 °C
   c) Reactor pressure: 760 mmHg
   d) Barometric pressure: 753 mmHg
   e) One revolution (1 L) of wet test meter takes 130 sec
   f) Catalyst volume: 3 ml
   g) Catalyst weight taken for experiment: 4.52gm
   h) Vapor pressure of water at 27°C : 26.7 mmHg
   i) Room temperature: 27.5 °C

2. Saturated gaseous flow rate at NTP

$$= \frac{1L \times 3600\,\mathrm{sec}}{130\,\mathrm{sec} \times 1hr.} \times \frac{273}{300} \times \frac{753}{760} \times \frac{1gm-mole}{22.4litre} = 1.115\frac{moles}{hr.}$$

3. Dry gas flow rate at NTP

$$= 1.115\left(\frac{753-26.7}{753}\right) = 1.0755\frac{gm-moles}{hr.}$$

4. Response factor of gas chromatograph: Molecular sieve column

Response Time	Components	Area a_i	Actual compositions b_i	$\frac{a_i}{c_i}$	Reference component's $\frac{a_r}{c_r}$	Response Factor $F = \frac{a_i/c_i}{a_r/c_r}$
1.02	H_2	2329	48.27	48.25	19350	401.04
1.577	Ar	105073	5.43	19350		1.0
2.165	N_2	549789	31.8	17288		1.1193
3.797	CH_4	129072	8.37	15420		1.2550
5.133	CO	109169	6.13	17808		1.0866

5. Sample gas analysis:

From Porapak column data

$$CO_2 = \frac{1.4 \times 199358}{28021} = 9.96\%$$

So, $H_2 + Ar + CO = (100-9.96) = 90.04\%$

From molecular sieve column data responded area:

$H_2 = 2178 \times 401.04 = 873465 = 39.38\%$

$Ar = 1311020 \times 1 = 1311020 = 59.11\%$

$CO = 30756 \times 1.0866 = 33419 = 1.51\%$

Actual composition:

$H_2 = 0.3938 \times 90.04 = 35.45\%$

$Ar = 0.5911 \times 90.04 = 53.22\%$

$CO = 0.151 \times 90.04 = 1.357\%$

6. Conversion of CO

$$\%conversion = \frac{9.96}{9.96 + 1.357} = 88.09\%$$

7. Rate of reaction:

$$Rate = \frac{1.0755 \times 0.0996}{4.52} = 23.70 \times 10^{-3}$$

$$Rate \times 1000 = 23.70 \frac{gm-mole}{gm-catalyst.hr}$$

8. Calculation of Space velocity:

Volume of dry gas at 753 mmHg and 200°C

$$= 1.0755 \frac{gm-mole}{hr.} \times \frac{22.4L}{1gm-mole} \times \frac{473}{273} \times \frac{753}{760} = 41.36 \frac{L}{hr}$$

Volume of steam at 753 mmHg and 200°C

$$= 35 \frac{ml}{hr} \times \frac{1mole}{18ml} \times 22.4 \frac{L}{mole} \times \frac{473}{273} \times \frac{753}{760} = 74.8$$

Total volume of feed at operating conditions:

$$= 41.36 + 74.8 = 116.16 \frac{L}{hr}$$

Space velocity:

$$\frac{116.16 \times 1000}{3} = 38720\ h^{-1}$$

APPENDIX D

Calculated Data

Table D.1: Laboratory Catalyst Preparation Methods and Their Comparison with Commercial Method

Composition of Prepared and Industrial Catalysts: CuO = 41%, ZnO = 31 %

Experimental Conditions are shown in Table 4.1

Methods .	Weight of Catalyst (gm)	Conversion of CO, %	Rate × 1000 (g.mole CO converted/ (g.cat.hr.))
M1	4.52	88.1	23.7
M2	4.12	70.2	17.2
M3	3.98	82.3	22.4
M4	4.02	74.0	19.8
Indus.	3.62	92.2	27.1

Table D.2: Effect of Catalyst Compositions on the Activity of Catalyst Prepared By Method-1 and Its Comparison with Industrial Catalyst

Experimental conditions are given in Table 4.1

Sample. No.	Compositions of Catalysts % wt.			Wt. of Catalyst (gm)	Conversion of CO, %	Rate × 1000 (g.mole CO converted/(g.cat.hr.))
	CuO	ZnO	Al_2O_3			
1	41	31	28	4.52	88.1	23.7
2	35	53	12	4.37	84.5	25.6
3	25	43	32	4.23	78.2	20.8
4	15	43	42	4.01	63.6	17.2
Indus.	41	31	28	3.62	92.2	27.11

Table D.3: Effect of Catalyst Compositions on the Activity of Catalyst Prepared By Method-2 and Its Comparison with Industrial Catalyst

Experimental conditions are given in Table 4.1

Samp. No.	Compositions of Catalysts % wt.			Wt. of Catalyst (gm)	Conversion of CO, %	Rate × 1000 (g.mole CO converted/(g.cat.hr.))
	CuO	ZnO	Al_2O_3			
1	41	31	28	4.12	70.2	17.2
2	41	28	31	4.36	74.4	19.8
3	41	47	11	3.89	59.2	20.2
4	35	53	12	4.08	67.3	19.0
Indus	41	31	28	3.62	92.2	27.11

Table D.4: Effect of Catalyst Compositions on the Activity of Catalyst Prepared By Method-3 and Its Comparison with Industrial Catalyst

Experimental conditions are given in Table 4.1

Samp. No.	Compositions of Catalysts % wt.			Wt. of Catalyst (gm)	Conversion of CO, %	Rate × 1000 (g.mole CO converted/(g.cat. hr.))
	CuO	ZnO	Al_2O_3			
1	41	31	28	3.98	82.3	22.4
2	35	53	12	4.29	78.1	20.2
3	25	43	32	3.78	79.6	18.03
4	15	43	42	3.69	63.5	11.8
Indus	41	31	28	3.62	92.2	27.11

Table D.5: Effect of Catalyst Compositions on Activity of Catalyst Prepared By Method-4 and Its Comparison with Industrial Catalyst

Experimental conditions are given in Table 4.1

Sample. No.	Compositions of Catalysts % wt.			Wt. of Catalyst (gm)	Conversion of CO, %	Rate × 1000 (g.mole CO converted/(g.cat.hr.))
	CuO	ZnO	Al_2O_3			
1	41	31	28	4.02	74.0	19.8
2	41	45	14	4.11	78.8	21.1
3	41	25	34	3.76	57.3	16.5
4	35	53	12	3.95	64.5	17.2
Indus	41	31	28	3.62	92.2	27.11

Table D.6: Comparison of Short-Term Stability Study of the Prepared (M1 and M3) and Industrial Catalysts

Reaction and reduction conditions are described in Table 4.1
Catalysts Volume = 3 ml
Catalyst formulation pressure for prepared catalysts = 700 kg/cm^2

Exp. Run	Exp. time, days	Conversion, % mole			Rate×1000(g-mol CO converted/gm. cat/hr)		
		M-1	M-3	Indus.	M-1	M-3	Indus.
1	1st	74.3	82	94.6	24.11	22.1	27.11
2	2nd	73.0	82.3	95.7	24	21.5	28.01
3	3rd	75.2	84.5	92.5	24.3	22	26.05
4	4th	72.9	78.3	93.4	24.01	21.13	27
5	5th	69.8	80.0	93.0	24	20	26.18
6	6th	69.0	78.5	89.5	23.05	19.05	26.26
7	7th	68.7	79	96.7	21.17	19.8	26.12
8	8th	70.0	78.5	92.0	22	20	26.1
9	9th	71.1	79.0	92.3	22	19.5	26.23
10	10th	67.4	76.1	88.7	20	19.5	25.8
11	11th	68.0	77.2	91.0	21.37	19	26
12	12th	69.5	77.6	91.1	21.51	19.2	26
Wt. of Catalysts (gm)		4.59	4.4215	3.6166	4.590	4.4215	3.6166

Table D.7: Long-Term Stability Study of the Prepared (M3) and Industrial Catalysts.

Reduction and reaction conditions for the test of industrial catalyst at laboratory conditions (mesh size 16-25) are shown in Table 4.1, Space velocity = 9300-9600 h^{-1} for reaction and 1600-2500 h^{-1}, CuO = 41%, ZnO = 31%

No. of Obs.	Time , Weeks	% Conversion of CO		Rate * 1000 (g-mole CO converted/ (g.cat.hr))	
		Mesh Size: 4-6		Mesh Size: 4-6	
		Prepared Catalyst (M3)	Industrial Catalyst ICI 83-3	Prepared Catalyst (M3)	Industrial Catalyst(ICI 83-3)
1	1st	87.2	72.4	4.51	3.66
2	2nd	86.5	73.0	4.51	3.70
3	3rd	85.0	72.7	4.48	3.68
4	4th	85.0	72.5	4.49	3.67
5	5th	85.0	72.1	4.48	3.65
6	6th	84.8	72.1	4.48	3.65
7	7th	83.6		4.46	
8	8th	82.1		4.42	
9	9th	82.0		4.4	
10	10th	80.4		4.39	
11	11th	78.5		4.34	
12	12th	78.0		4.31	
Wt. of Catalyst		13.4793	10.8404	13.4793	10.8404

Table D.8: Standard Conditions for the Characterization of Low Temperature Shift Catalysts

	Name of Parameters	Conditions
1.	Catalyst Particle Size, Mesh	30-34
2.	Catalyst Weight, gm	1.0-0.1
3.	Sample Holder	Micro Sample U-tube
4.	Vacuum drying prior to degassing	2 hrs at 120°C
5.	Degassing Conditions a) Flow rate of He or He-N_2 mixture, ml/min b) Duration, h	 14-16.5 3-4
6.	Method of surface area measurement	Multipoint
7.	Adsorbate	N_2
8.	Adsorption temperature , °C	-196