

## Chemical Kinetics of CO oxidation

### 10. General

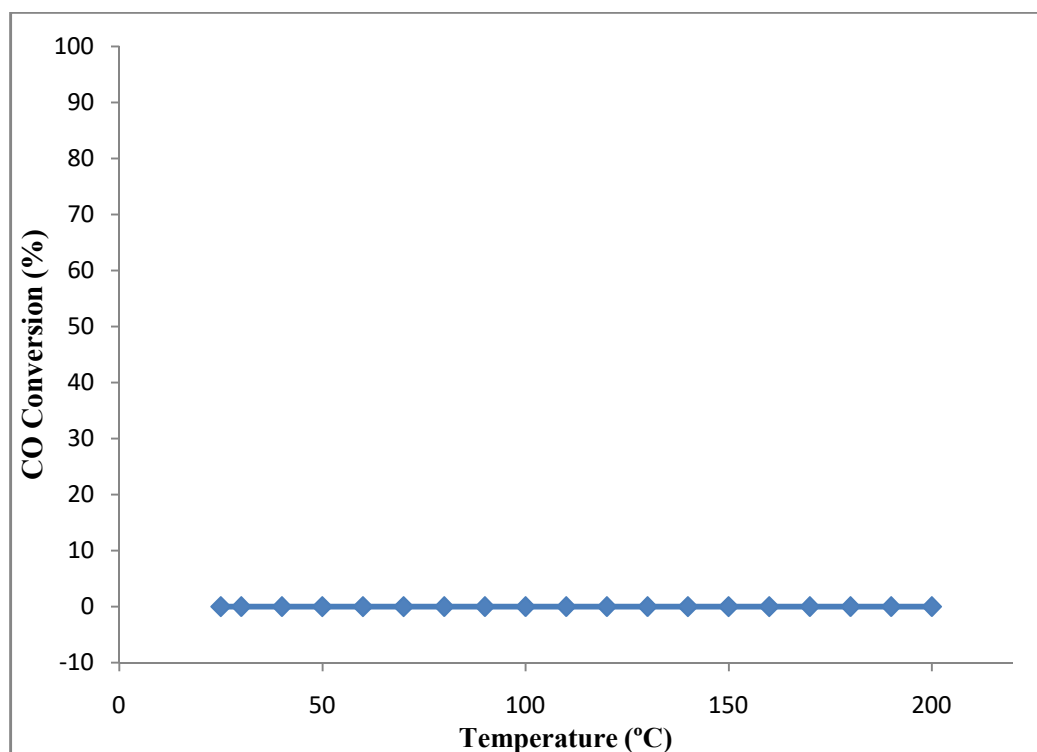
The heterogeneous reactions are the crucial reactions in the formulation and evaluation of the catalysts. The reaction of a gas with a solid usually proceeds as topo-chemical reaction, i.e., interface between the solid catalyst and the gaseous reaction mixture. Chemical kinetics establishes the factors, which influences the rate of the reaction under consideration and provides explanation for the measured value of rate and leads to the rate equations, which is useful in the reactor design. The mechanism of the reaction and the rate expression depend much on the catalyst used and their structure and properties of their surfaces. The apparent rate may be influenced by the physical texture of the catalyst [Li *et al.*, 2007]. The porous catalyst particle has a great advantage is that the active catalyst surface is freely accessible to the reactants and the physical resistances to the interface and the inside of pores are reduced to minimum. It may be pointed out that the thermal effects during the reactions cause temperature distribution, both in single particle and also in catalyst bed. The meaningful kinetic data can be obtained from a packed bed reactor, only if the flow pattern within the reactor resembles plug flow. Plug flow behavior provides a simple relationship between the feed rate and the rate of reaction [Jones *et al.*, 2008].

In present study, the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by the precipitation-deposition method, and their performance for CO oxidation was evaluated at low temperature. The 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst being produced under the oxygen-rich atmosphere conditions and its confirmation of the retardation of copper oxide and reduction of manganese phases under the oxygen-deficient conditions, to produce residual Cu<sub>2</sub>O and Mn<sup>2+/3+</sup> oxide phases. The success of

3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has encouraged a big deal of fundamental work devoted to instructive the role played by each element and the nature of active sites. The novel redox method allowed for the room temperature synthesis of amorphous 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with high surface area and high catalytic activity. A better tool for measuring the performance of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for CO oxidation was reported the activation energy of the process. The activation energy data was enviable for the modeling and design of the catalytic converters. It was applicable to develop kinetic expressions for catalytic oxidation of CO because it was implemented into CFD models for reactor design and optimization. The chemical kinetics established the factors, which influences the rate of reaction under consideration and it provides clarification for the measured value of rate and leads to the rate equations, which was valuable in reactor design. The mechanism of the reaction and the rate expression depend much on the types of catalysts was used and their structure and surfaces properties.

### 10.1 Blank experiment

A blank experiment was carried out with alpha-alumina only in place of the catalyst. At bed temperature increase up to 200°C practically no oxidation of CO has been observed under the experimental conditions. In Figure 10.1, we have observed that there will be no conversion of CO has occurred at the increasing of temperature in catalytic experiments. From the blank test we have measured the performance of reactor in the absence of a catalyst for CO oxidation and the increasing of temperature does not show any activity for CO oxidation. Thus, the catalytic effect of the reactor wall and the alumina used as diluents can be neglected within the experimental conditions. Finally, we get that the alumina support was inactive for CO oxidation under the conditions was studied.

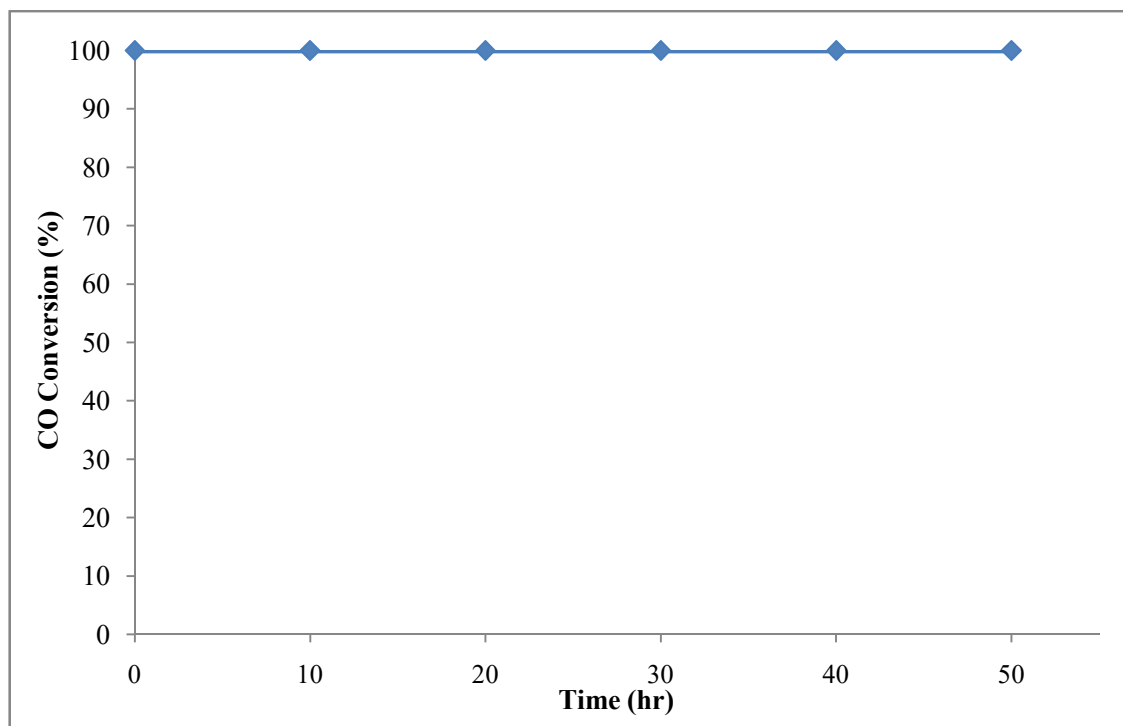


**Figure 10.1:** Blank test for CO oxidation

## 10.2 Stability test

The stability test of 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst was conducted at 55°C for the oxidation of CO in a continuous running for 50h under the earliest mentioned experimental conditions. The result revealed that practically no deactivation of the 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst has occurred in the experimental conditions. In the Figure 10.2 we have seen that the 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst was stable for 50h under the continue running process. The extraordinary performance of 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst produced by reactive calcination (RC) for CO oxidation was associated with the modification in intrinsic textural, morphological characteristics such as surface area, crystallite size and particle size of the catalyst. The performance of catalyst was judged by their activity, selectivity and stability. The objective of this study was to evaluate the stability of 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst as well as their importance of CO<sub>2</sub> formation. The silver promotion has improved the stability of

$\text{Cu}_1\text{Mn}_8$  catalyst and they create ideal conditions for the catalyst even enhances the life of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst by saving them from poison. An addition of Ag into the  $\text{Cu}_1\text{Mn}_8$  catalyst, therefore no further deactivation of the catalyst has been observed. The dynamics and stability of the catalyst in the catalytic reactors were depending upon, the optimal starting and operation conditions.



**Figure 10.2:** Stability test of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for oxidation of CO

The interaction (synergetic effects) of different metal oxides dispersed on the surface reduces the deactivation of the catalyst. Higher activity, stability in both oxidizing and reducing atmospheres was supporting on high geometric surface area substrates with minimal pressure drop.

### 10.3 Kinetic study of CO oxidation over 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

The apparent rate may be influenced by the physical texture of the catalyst. The porous catalyst particles has a maximum advantage is that it contain active surface area for freely accessible to the reactants and the physical resistances to the interface therefore

inside the pores are reduced to the minimum. It may be pointed out that the thermal effects during the reaction causes the temperature distribution, both in single particle and also in catalyst bed. The expressions relating to power functions of concentrations or partial pressures of reactants and products are temperature dependent kinetic constant often fit the data. The general form of these rate expressions is given by Eq.10.1 below:

$$\text{Rate of reaction} = (\text{Kinetic term}) (\text{Driving force}) / (\text{Resistance term}) \text{----- (10.1)}$$

The ratio of length and diameter of the reactor particle size used in the present study was 30 and 6 respectively; it can be safely assumed that the flow in the packed bed reactor satisfies the situation (necessary to be fulfilled) for plug flow to exist in the reactor. The reactor to particle diameter ratio of 60-80 can be more than adequate to assume a flat velocity profile across the reactor diameter. The catalyst bed length to particle diameter ratio of 50-80 allows one to neglect (without introducing significant error) the axial dispersion in the catalyst bed. The 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst was selected for the kinetics studies because it shows the maximum activity and slowest deactivation rate in comparison to other catalysts. In this regard, a few kinds of literature have been reported in the kinetic study of the catalytic oxidation of CO over supported CuMnOx catalyst.

The kinetic study was done in the stable area of catalyst; therefore, we obtain any kinetic model. The experiment of stability study was carried out in the same continuous-flow, fixed-bed reactor. To make sure the essential reaction kinetics was measured without the mass transfer resistance; the internal and external dispersion effects must be removed. The same amount of catalysts with different particle size was used to test the internal mass transfer resistance. The variation of CO concentration was measured using a reactor at different temperatures. Among the power-law, reaction rate law models

frequently have been found to be sufficient enough for preface studies. The reported activation energies of different catalysts were mentioned in Table 10.1. For comparison, the activation energy determined in the present study was also reported in this table. The basic reason, which leads to the inconsistencies, was associated with the types of catalyst and the experimental conditions. The present work was dedicated for the first time to study the kinetics of the air-oxidation of diluted CO over the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at various temperatures (25-30°C). Efforts have been made to fit the CO oxidation data to power law rate equation. In our experiments, the influence of oxygen can be neglected, when it present in great excess, therefore, its concentration remains constant in all the experiments.

**Table 10.1:** Activation energy for CO oxidation over different catalysts

S.N.	Catalyst	Temperature (°C)	Activation energy (kJ/mol)	References
1.	Au/TiO <sub>2</sub>	-70°C to 60°C	30	Date and Haruta 2001
2.	Pt-Rh/Al <sub>2</sub> O <sub>3</sub>	193°C to 234°C	83.6	Granger <i>et al.</i> , 2001
3.	Silica	400°C to 560°C	109.5	McCormick <i>et al.</i> , 2002
4.	CuMnOx	60°C to 110°C	64.08	Li <i>et al.</i> , 2007
5.	CuMnOx	20°C to 100°C	67.82	Xia <i>et al.</i> , 1999
6.	CoMnOx	20°C to 100°C	75	Xia <i>et al.</i> , 1999
7.	AgMnOx	20°C to 100°C	41	Xia <i>et al.</i> , 1999
8.	Au/CeO <sub>2</sub>	50°C to 190°C	76	Luengnaruemitchai <i>et al.</i> , 2004
9.	CoOx	240°C to 280°C	40	Youn and Chun 2008
10.	Au/CoOx	240°C to 280°C	44	Chen <i>et al.</i> , 2003
11.	Pt/Al <sub>2</sub> O <sub>3</sub>	50°C to 60°C	56.5	Newton <i>et al.</i> , 2016
12.	Pt/SnOx	70°C to 80°C	31	Schubert <i>et al.</i> , 2001

13.	Pt-SnOx	100°C to 120°C	35	Baltacioglu <i>et al.</i> , 2007
14.	Pt-Co-Ce/ Al <sub>2</sub> O <sub>3</sub>	100°C to 110°C	37.73	Ozyonum <i>et al.</i> , 2007
15.	Au/TiO <sub>2</sub>	-10°C to 65°C	34.33	Haruta <i>et al.</i> , 1993
16.	Au/ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	-10°C to 65°C	35.16	Haruta <i>et al.</i> , 1993
17.	Au/Co <sub>3</sub> O <sub>4</sub>	-10 to 65°C	16.32	Haruta <i>et al.</i> , 1993
18.	Au/Mg(OH) <sub>2</sub>	100°C	22.50	Cunningham <i>et al.</i> , 1999
19.	Pd(111)	47°C	16.23	Piccinin and Stamatakis 2014
20.	Pd(100)	25°C	19.25	Santra and Goodman 2002
21.	Pd(111)	25°C	14.56	Santra and Goodman 2002
22.	Au/TiO <sub>2</sub>	25°C	27.69	Santra and Goodman 2002
23.	Au/TiO <sub>2</sub>	-25°C to 30°C	16.69	Guzman and Gates 2004
24.	Pt(100)	45°C to 125°C	22.15	Berlowitz <i>et al.</i> , 1988
25.	Pd(110)	45°C to 125°C	26.65	Berlowitz <i>et al.</i> , 1988
26.	Ir(111)	45°C to 125°C	29.85	Berlowitz <i>et al.</i> , 1988
27.	Ir(110)	45°C to 125°C	33.65	Berlowitz <i>et al.</i> , 1988
28.	Au/TiO <sub>2</sub>	-30°C to 65°C	13.25	Okumura <i>et al.</i> , 1998
29.	Au/Fe <sub>2</sub> O <sub>3</sub>	-30°C to 65°C	19.89	Okumura <i>et al.</i> , 1998
30.	Au/Co <sub>3</sub> O <sub>4</sub>	-30°C to 65°C	17.65	Okumura <i>et al.</i> , 1998
31.	Au/NiO	-30°C to 65°C	21.45	Okumura <i>et al.</i> , 1998
32.	Pt(111)	30°C	24.11	Campbell <i>et al.</i> , 1980

33.	Fe <sub>2</sub> O <sub>3</sub>	300°C	60.70	Li <i>et al.</i> , 2003
34.	Pt(100)	117°C	56.45	Cant <i>et al.</i> , 1995
35.	Au <sub>5</sub> AgZr <sub>14</sub>	-20°C to 50°C	29.65	Baiker <i>et al.</i> , 1995
36.	Au <sub>5</sub> FeZr <sub>14</sub>	-20°C to 50°C	22.45	Baiker <i>et al.</i> , 1995
37.	Nd <sub>0.75</sub> Sr <sub>0.25</sub> Co O <sub>3-y</sub>	100°C to 230°C	64.9	Jung <i>et al.</i> , 1996
38.	Nd <sub>0.5</sub> Sr <sub>0.5</sub> Co O <sub>3-y</sub>	100°C to 230°C	66.9	Jung <i>et al.</i> , 1996
39.	Nd <sub>0.25</sub> Sr <sub>0.75</sub> Co O <sub>3-y</sub>	100°C to 230°C	62.3	Jung <i>et al.</i> , 1996
40.	Cu(100)	200°C to 270°C	93.25	Favaro <i>et al.</i> , 2017
41.	3%AgCuMn <sub>8</sub> O <sub>x</sub> /60% $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	25°C -30°C	50.26	Present Study

Efforts have been made to fit the CO oxidation data to power law rate equation. Early studies indicated that the catalyst initially oxidized CO before it oxidized by air, and this was indicative of a Mars van Krevelen-type mechanism, which has subsequently found support. A Langmuir–Hinshelwood-type mechanism between the adsorbed oxygen and CO has also been proposed, and it was not clear if either operates exclusively or there was a combination of both. The oxidation of CO by the Mars van Krevelen mechanism would explain the relation between the easiness of catalyst activity and reducibility. The oxidation of CO over 3%AgCuMn<sub>8</sub>O<sub>x</sub>/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst could be described very well by Langmuir-Hinshelwood model, in which molecularly adsorbed CO reacts with the dissociative adsorbed oxygen in the first order reaction.

The amount of reactant consumed and product formed can be monitored as a function of the surface composition of the catalyst. In contrast, a surface composition test, the catalyst composition does not modify significantly because many surface molecules were very much lower than the number of surface active sites/species. Thus, in a multi-



surface experiment, it was probable to observe that the whole dependence of the catalyst activity as a function of the catalyst composition or amount of available active sites. A complete analysis of these dependency enables the sites to be illustrious kinetically on the progressive activity changes (i.e. decreases) as all the sites become occupied. A power-function rate expression dependence on CO and oxygen present in air was obtained by the low-temperature CO oxidation. On comparison amongst the values of activation energies; it became clear that the novel 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst, used in this study, was one of the most active catalysts. In spite of the considerable progress in CO oxidation studies and the complete literature, there was a still uncertainty concerning the corresponding kinetic equations. The aim of this work to investigated the intrinsic reaction kinetics of CO oxidation on the 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst.

### 10.3.1 Mechanism of CO oxidation over 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst

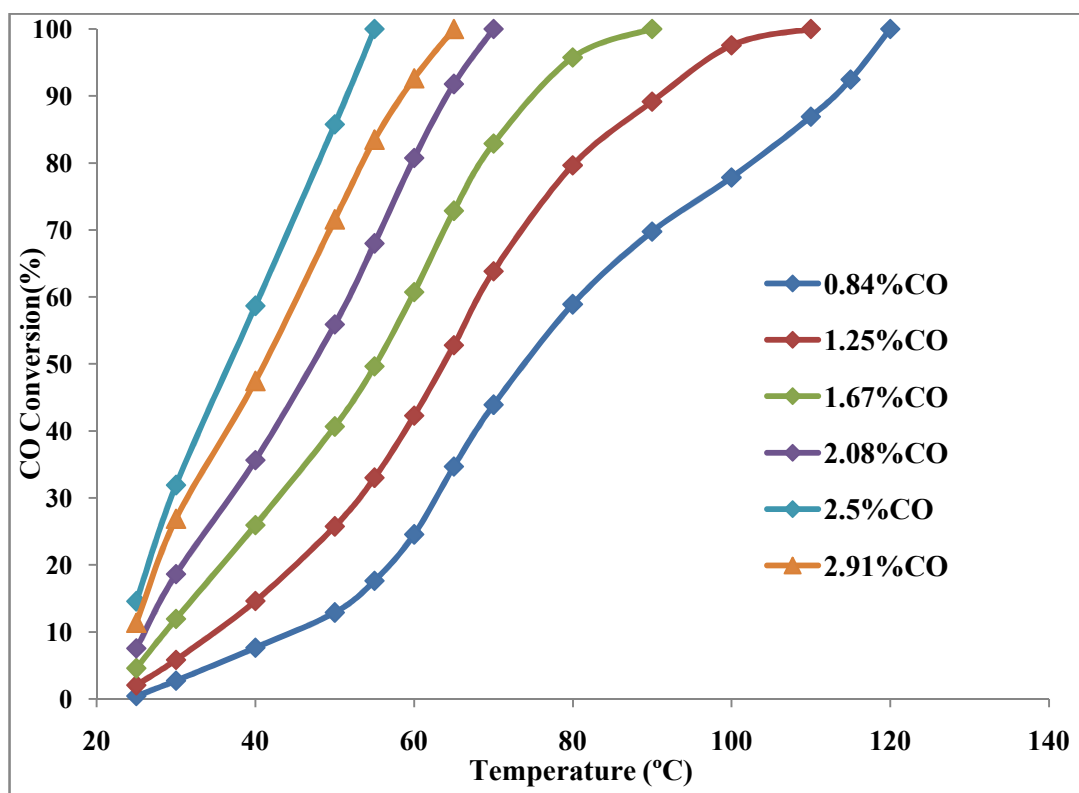
The low-temperature catalytic oxidation of CO was a significant reaction and it's applied in many different fields. The efficiency of solid catalysts for reactions with stable molecules was depending upon the chemisorptions. The chemisorptions of the reacting gasses was an important step, which increase the concentration of reactant on the catalyst surfaces which inducing the adsorbed molecules processing on high energy to be accessible to chemical reactions. The distinct reaction mechanisms were consistent with the observed kinetics. In the CO oxidation process, the oxygen was first adsorbed on the 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst surface with the energy of activation. When the temperature was high an adequate amount so that the adsorption of oxygen reaches enough proportions, therefore any CO passing over the catalyst surfaces either reacts directly with the adsorbed oxygen or else is first adsorbed and then reacts, after

which the CO produced being desorbed. The similar nature of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by the redox method and it could be one of the major factors contributing to their high catalytic activity. The precipitation-deposition method was allowed for the preparation of amorphous catalysts with high surface areas and high catalytic activity.

The kinetic parameters for the CO oxidation was analysis by the following product formation as a function of CO under the reaction conditions required for a differential operating regime (reactants conversion 15% at any temperatures used). In these experiments, carbon dioxide (CO<sub>2</sub>) was referred as product and carbon monoxide (CO) was referred as an inlet. Before the kinetic study, the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was diluted with inert solid particles of  $\alpha$ -alumina to avoid the formation of hot spots in catalytic bed as well as increase the heat transfer area of the catalyst bed. A blank reaction ( $\alpha$ -alumina only, 1mL) was bringing out earlier to conducting the kinetic study and do not illustrate any activity, nor show any homogeneous combustion of CO occur. The analytic test of external and internal mass transfer limitations was also carried out before conducting the kinetic study and shows that the reaction was free of external and internal mass transfer limitations. The effect of external intra-particle mass transfer and external film diffusion was avoided on the oxidation reaction by using fine particle (40-100 mesh) of the catalyst. To be on the safe side, the catalyst with the smaller particle size was used for collecting the kinetic data. The kinetic data for the oxidation of CO over the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at different temperatures was shown in the Figure 10.3. An effort was made to fit the kinetic data to power-law rate expression as preferred by Levenspiel [Schubert *et al.*, 2001].

### 10.3.2 Kinetic study of 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at different flow rate

The significant kinetic data can be obtained from a packed bed reactor, only if the flow pattern within the reactor resembles plug flow. The plug flow behavior provides a secure connection between the feed rate and the rate of reaction. In the present study, the different concentration of CO present in air flows through the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and their activity for CO oxidation was illustrated in the Figure 10.3 and also mentioned in the Table 10.2.



**Figure 10.3:** CO conversion vs temperature for varying CO concentration in air

In the activity test, we have to take 100mg catalyst with CO flow rate maintained (0.5-1.75ml/min) and air flow rate maintained (58.25-59.5ml/min). The total flow rate of (CO + Air) has been maintained 60ml/min at the room temperature (25°C). The percentage of CO present in air at the activity test was varying from 0.84% to 2.91%. Each experiment was performed three times for measuring the average value of CO oxidation, and the average results were plotted. It was important to determine the

catalyst bed temperature gradients. The comparison of inlet and bed temperature for all the runs and the axial bed temperature profiles of selected runs showed that under most operating conditions, the reactor was sufficiently isothermal for this study.

**Table 10.2:** CO conversion vs temperature for various CO concentration in air

CO in air (%)	T <sub>25</sub> <sup>o</sup> C	T <sub>30</sub> <sup>o</sup> C	T <sub>35</sub> <sup>o</sup> C	T <sub>40</sub> <sup>o</sup> C	T <sub>45</sub> <sup>o</sup> C	T <sub>50</sub> <sup>o</sup> C	T <sub>55</sub> <sup>o</sup> C
0.84%	0.45%	2.75%	5.25%	7.65%	10.04%	12.9%	17.65%
1.25%	2.05%	5.85%	10.35%	14.65%	18.45%	25.75%	33%
1.67%	4.58%	11.95%	18.08%	25.95%	32.35%	40.65%	49.65%
2.08%	7.57%	18.65%	27.55%	35.65%	46.70%	55.90%	67.97%
2.5%	14.56%	31.90%	42.30%	58.65%	71.55%	85.76%	100%
2.91%	11.40%	26.90%	35.65%	47.43%	58.70%	71.55%	83.45%

The initial rate of CO oxidation was individually extracted from the crucial kinetic data obtained in experimental run under the conditions where the complete CO oxidation was achieved. The CO conversion increases with the increasing of CO concentration because the speed of CO oxidation was expressed as the change in CO concentration over a certain period of time. When the CO concentration has increases, therefore more CO molecules present in a reaction, it causes more collisions as occurs. After the more collisions of CO molecules the faster reaction proceeds, therefore the rate of reactions has increases. The successful collisions of CO molecules have produced enough energy and this energy also known as activation energy. The increasing of reaction temperature, thus bringing about more successful collisions, it also causes increases the rate of reaction. The speed of CO molecules collision with the increasing of temperature produces more energy and this energy sufficient to reach the  $E_a$ , it causes increases the overall reaction rate. The rate of chemical reaction was measured by the decrease in

concentration of a reactant or an increase the concentration of a product in a unit of time. The CO conversion measured at the time on stream of 120 min (after the reactant gasses were introduced into the system), which should be sufficient to reach the steady state conditions. From the Figure 10.3 we have observed that the 2.5% CO in air was the optimum composition for its total conversion CO into CO<sub>2</sub> at the lowest temperature of 55°C. After increasing the CO percentage beyond (2.5%), the oxidation of CO has been decreased. At the high temperatures, the chemisorptions would be expected to reduce with increasing temperature and reduce the inhibition effect.

### 10.3.3 Weight hourly space velocity over 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst

In this experimental study, the reaction conditions have been completely satisfied, and it implies that the reactor use behaving as an ideal plug flow reactor. The rate of CO oxidation was evaluated using the differential method. The kinetic experiments repetitive for (2.5% CO in air) feed composition at a temperature range (25-30°C), to ensure that the data correspond to the linear change of CO conversion (X<sub>CO</sub>) with space-time (W/F<sub>CO</sub>) in the initial rates region in which the reaction was kinetically controlled. Therefore, the rate of CO oxidation in the plug flow reactor as given as Eq. 10.2.

$$-r_{CO} = dX_{CO}/d(W/F_{CO}) \text{ ----- (10.2)}$$

Where X<sub>CO</sub> was the conversion of CO and W/F<sub>CO</sub> was the weight hourly space velocity (WHSV). The constants in each model equation were combined as much as possible to minimize the number of unknowns and, therefore, the number of experimental data required. The weight of catalyst was 100mg and flow rate was fixed at 1.50ml/min (2.5%CO in air) and temperature varies from (25°-55°C). The temperature was fixed at different flow rate of CO at (0.75-1.75ml/min) in reactive calcination conditions.

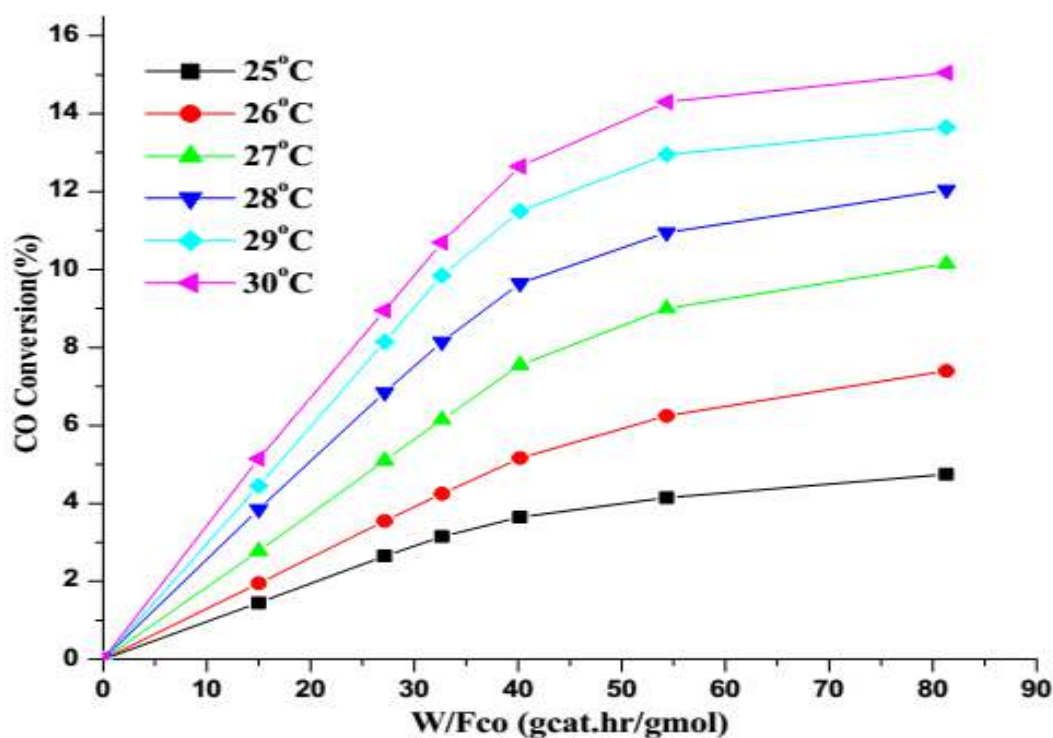


Figure 10.4: CO conversion  $X_{CO}$ (%) vs  $W/F_{CO}$ (g-cat.hr/gmol) at various temperatures

Variation in  $W/F_{CO}$  was made by varying the composition of CO in the feed and keeping the other parameters make constant. The upper limit of CO conversion for each run was restricted below 15% to decrease the heat and mass transfer effects and realize the performance of the differential reactor. The mathematical models described the chemical reaction kinetics and understand their processes. These models can also be use in the design or modification of chemical reactors to optimize the product yield. Chemical kinetics was frequently validated and explored through modeling in specialized packages as a function of normal differential equation-solving and curve-fitting.

**Table 10.3:**  $X_{CO}(\%)$  vs  $W/F_{CO}$  (g-cat.hr/g.mol) at various temperatures

W/F <sub>CO</sub> (g-cat. hr/ gmol)	Conversion at temperature					
	25(°C)	26(°C)	27(°C)	28(°C)	29(°C)	30(°C)
5.0	1	1.65	2.45	3.60	4.25	4.85
10	1.95	2.85	4.35	6.15	7.25	8.15
15	2.85	4.03	6.15	8.15	9.45	10.70
20	3.56	5.16	7.55	9.65	11.88	12.65
25	4.15	6.25	9.01	10.95	12.15	14.30
30	4.75	7.40	10.15	12.05	13.85	15.00

The rate of reaction at any conversion can be obtained by measuring the slope on the curve, which was obtained by plotting  $X_{CO}$  versus  $W/F_{CO}$  values and mentioned in Table 10.3. The rate of CO oxidation according to power law model was

$$-r_{CO} = k (C_{CO})^n (C_{O_2})^m \text{-----} (10.3)$$

Where  $k$  was a reaction rate constant, and  $C_{CO}$  was the concentration of CO, and  $C_{O_2}$  was the concentration of oxygen. In the present study a lean mixture of reactant, 2.5% CO in the air was used; therefore oxygen in the huge excess was present in air, and the rate expression reduces to the pseudo  $n^{th}$  order Eq. 10.4.

$$-r_{CO} = k(C_{CO})^n \text{-----} (10.4)$$

$$\text{or } \ln(-r_{CO}) = \ln k + n \ln C_{CO} \text{-----} (10.5)$$

The rate of reaction ( $-r_{CO}$ ) at a different degree of conversion for each temperature was determined by measuring the slope of the curves given as Eq.10.4. In each experiment, CO conversion ( $X_{CO}$ ) data taken at steady feed composition by varying space-time ( $W/F_{CO}$ ) were used to confirmed the linear change characteristic of the initial rates

region; with linear regression constants,  $R^2$  was used in the subsequent individual rate calculations. This means that the regression equation was reliable. It may be distinguished that the reactant mixture was lean (2.5%) and therefore, the changes taking place in the volume due to the reaction can be neglected without introducing any significant error. Therefore, we assume that the constant density system due to the negligible value of variable density factor ( $\epsilon$ ). Under this condition, the following expressions Eq.10.5 will be valid.

$$C_{CO} = C_{CO(inlet)}(1 - X_{CO}) \text{ ----- (10.6)}$$

Where  $C_{CO(inlet)}$  and  $C_{CO}$  was the concentration of CO at the inlet and outlet of reactor respectively. The  $C_{CO(inlet)}$  can be calculated assuming ideal gas law then  $C_{CO}$  was determined by using Eq.10.6. The rate of CO oxidation on 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst surface has proceeds through two successive stages; first reduction of catalyst surface by CO with the formation of CO<sub>2</sub> followed by re-oxidation of reduced surface by gaseous oxygen. The study on the kinetic aspects of the reaction was carrying out for the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst surface, which exhibited the best performance in CO oxidation and the rate expression was developed for the reaction. The order of reaction (n) was obtained from the values of slope line presence in a graph. The rate of the reaction going from CO to CO<sub>2</sub>, therefore the concentration of CO was decreasing and the concentration of CO<sub>2</sub> was increasing after passing through the 3%AgCuMn<sub>8</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst surfaces presence in the reactor.

#### 10.3.4 Reaction rate laws and power-law model

Among the reaction rate laws, the power-law model often has been found to be adequate enough for the preliminary studies. In the power law  $r_{CO}$  versus  $C_{CO}$  data were recognized at the constant temperature, n and k at that temperature can be determined



from a plot of  $\ln(r_{CO})$  versus  $\ln(C_{CO})$ . In the entire cases, a plot was finding to be linear (Figure 10.5). The kinetic parameters ( $k$  and  $n$ ) of the power law model for the oxidation of CO were determined from the slope and intercept of the plot. The order of reaction for CO oxidation on 3%AgCuMn<sub>3</sub>Ox/60% $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was found to be 0.997 i.e. first-order.

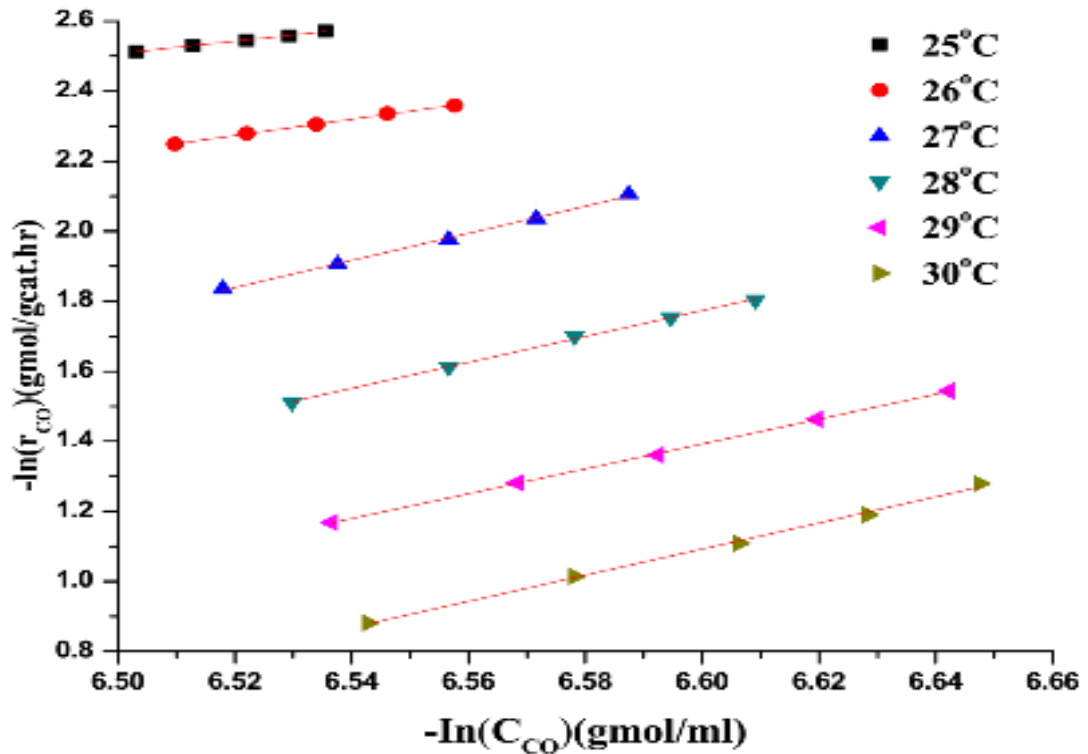


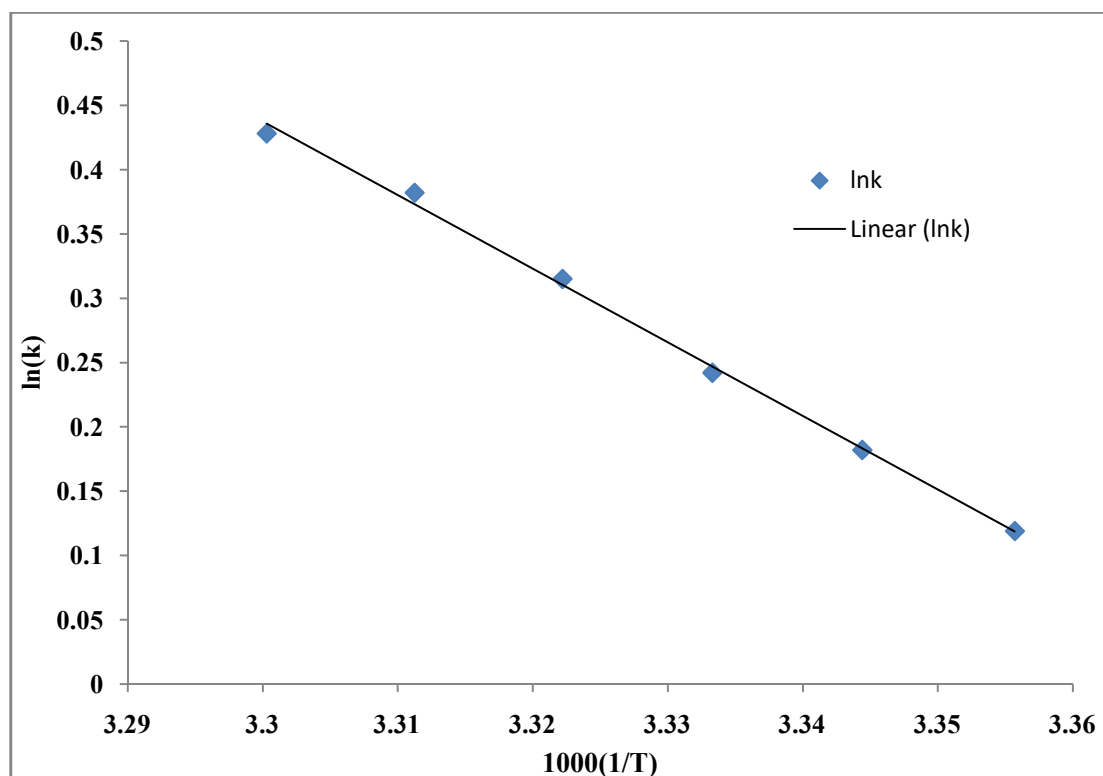
Figure 10.5: Plot of  $\ln(-r_{CO})$  vs  $\ln(-C_{CO})$

The areal rate of a given catalyst for CO oxidation was defined as the moles of CO oxidized per unit surface area of catalysts per unit time. The rate constant,  $k$ , was a function of temperature and can be expressed by Arrhenius Eq. 10.7.

$$k = A \exp(-E/RT) \text{----- (10.7)}$$

$$\text{or } \ln k = \ln A - E/RT \text{----- (10.8)}$$

The activation energy ( $E$ ) of the reaction can be evaluated from the slope of the plot  $\ln(k)$  versus  $1000(1/T)$  as per equations and plotted in Figure 10.6. The data of partial conversion of CO ( $X_{CO}$ ) into CO<sub>2</sub> under the conditions, when the catalyst exhibited steady performance, versus  $W/F_{CO}$  at six different temperatures.



**Figure 10.6:** Plot of  $\ln(k)$  vs  $1000(1/T)$

When a reaction has a rate constant that obeys Arrhenius' equation, a plot of  $\ln(k)$  versus  $1/T$  gives a straight line, whose gradient and intercept can be used to determine  $E_a$  and  $A$ . The Arrhenius' equation gives the dependence of the rate constant of a chemical reaction on the absolute temperature, a pre-exponential factor and other constants of the reaction. When a reaction has a rate constant that obeys Arrhenius' equation, a plot of  $\ln(k)$  versus  $1/T$  gives a straight line, whose gradient and intercept can be used to determine  $E_a$  and  $A$ . This equation has become so common in experimental chemical kinetics study so that it was taken to find out the activation energy of a reaction. With the help of this Arrhenius' equation, we have to calculate the minimum amount of activation energy ( $E_a$ ) at an absolute temperature ( $T$ ) required to complete oxidation of CO. The activation energy and pre-exponential factor ( $A$ ) of Arrhenius equation thus determined were given below:

$$\text{Activation energy (E)} = 50.26 \text{ kJ/mol}$$

$$\text{Pre-exponential factor (A)} = 7.165 \times 10^5 \text{ (g.mol)/(gcat.h)}$$

On the basis of experimental findings the rate of CO oxidation in the temperature ranges of (25-30°C) on the 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst can be expressed as follows:

$$\text{Rate } (-r_p) = 7.165 \times 10^5 \exp(-50261/RT)(C_{CO})^{0.99} \text{ g.mol/gcat.h}$$

The 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst plays an important role in the multi-phase catalytic system, namely, to capture the formed CO<sub>2</sub> to reduce the CO concentration over the active sites. These will be eventually facilitating the CO oxidation process for the bi-functional catalyst. It has been identified that the catalytic activity, heat adsorption and surface coverage were closely related with each other. The surface heterogeneity, heat of adsorption would be decrease with the increase of surface coverage. For CO oxidation through the 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst, the competitive adsorption between CO and CO<sub>2</sub> has resulted in less active site available for CO adsorption. This means that the surface coverage for CO adsorption will decrease, while the heat adsorption will increase. This was the reason why the temperatures and activation energies required for total oxidation of CO over the 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst.

#### 10.4 Concluding Remarks

The present work provided with a phenomenological outline to understand the reaction of 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst for CO oxidation. The oxidation of CO has been studied in a fixed bed plug flow reactor, and the kinetics data were collected under the condition of free heat and mass transfer limitations. Intrinsic rate of CO oxidation over 3%AgCuMn<sub>8</sub>Ox/60%γ-Al<sub>2</sub>O<sub>3</sub> catalyst was determined as a function of temperature range (25-30°C). The rate of CO oxidation was given by Rate  $(-r_p) = 7.165 \times 10^5 \exp(-50261/RT)(C_{CO})^{0.97}$  g.mol/gcat.h and the value of activation energy was found to be 50.26 kJ/mol, which was the least as compared to the activation energy for different

catalysts reported in the literature for CO oxidation. The obtained kinetics expression can be implemented into CFD models for reactor design and optimization of parameters.