

KINETICS AND REACTION MECHANISM OF LOW TEMPERATURE CARBON MONOXIDE OXIDATION ON OXIDE CATALYSTS

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(Communicated by Prof. S. K. Bhattacharyya, FNA)

(Received 29 November 1973; after revision 5 March 1975)

The kinetics of carbon monoxide oxidation was studied at low temperature (20°C, 40°C and 60°C) in a flow reactor on active oxide catalyst containing Iron, Copper, Manganese and Silver. Assuming a steady state, involving simultaneous reduction and oxidation of the catalyst, the following general rate equation was derived :

$$\gamma = \frac{K_1 K_2 p_{\text{CO}}^a p_{\text{O}_2}^b}{K_2 p_{\text{O}_2}^b + \alpha K_1 p_{\text{CO}}^a}$$

Theoretical rates were found to represent within narrow limits the experimental values. The activation energies of the individual steps were evaluated from Arrhenius plots. From an examination of the magnitude of the energy values it was concluded that the overall rate of the oxidation is not preferentially affected by either of the steps in the process.

INTRODUCTION

Heterogeneous oxidation of carbon monoxide by air on oxide catalysts provides a classic example in the field of catalysis and a voluminous literature has grown on the subject which has been reviewed from time to time (Katz 1953). The reaction has been studied from different stand points such as mechanism of reaction (Garner *et al.* 1935, 1952; and Stone 1962), kinetics of the process (Brooks 1967; Brittan *et al.* 1970; Alkhazov 1960; Tarama *et al.* 1960; and Syzdykbaova *et al.* 1967) with a view to derive a suitable kinetic model and to support the electronic theory of catalysis (Krylov 1970).

However literature is replete with conflicting as well as contradictory views not only on the reaction mechanism but also on basic parameters such as order of reaction (Brittan *et al.* 1970).

The primary objective of the present work was to study the kinetics of the reaction with a view to elucidate the reaction mechanism and to derive a kinetic model to explain the results.

EXPERIMENTAL

Apparatus: The reactions were carried out in a conventional type of flow reactor, care being taken to ensure that isothermal conditions are maintained during

the course of reaction. The heat of reaction being large, the catalyst bed was supported inside a large block of Aluminium so that heat of the reaction could be quickly dissipated. A hole of 1.5 cm diameter was drilled axially through the block to hold the catalyst particles. Stainless steel wire gauge was used to support the catalyst inside the block which was immersed in a liquid thermostat bath, the temperature of which was controlled within an accuracy of $\pm 1^\circ\text{C}$ by means of Sunvic energy regulator. A second hole in the block drilled parallel to the first one was utilized to insert a thermometer for measurement of reaction temperature. For test runs, a mixture of definite proportions of carbon monoxide, air and nitrogen was allowed to pass through a purifying train containing strong KOH and magnesium perchlorate before it entered the catalyst bed. The inlet and exit gases were analysed for CO and CO_2 in a standard Haldane gas analyser. The partial pressure of the reactants was varied by adding appropriate proportions of the constituents as well as by addition of nitrogen. In order to ensure that the kinetic data are meaningful, care was taken so that conversion did not exceed 10 per cent limit as otherwise drop in the partial pressure of the reactants in the vicinity of the catalysts might affect the differential rate.

Material: Carbon monoxide was prepared by the usual method of dropping formic acid over conc. sulphuric acid. Oxygen and Nitrogen were collected from cylinders after purification.

Of the several catalyst compositions examined, the one having the maximum activity had the following composition: $25\text{Fe}^{3+} : 25\text{Cu}^{2+} : 25\text{Mn}^{2+} : 25\text{Ag}^+ : 100$ kieselguhr. The catalysts were prepared by precipitation technique. A solution of 10 per cent sodium carbonate was added to a hot solution of the mixed nitrates of respective cations in definite proportions. The precipitate was washed free of alkali and made into a slurry with water. To a weighed amount of calcined kieselguhr was added water and converted into a slurry. The two slurries were then mixed with vigorous stirring in order to make a homogeneous mass. The product was dried in air oven at 110°C to 120°C and finally crushed to a size of 6 to 14 mesh B.S.S. The surface area of the catalyst determined by B.E.T. nitrogen adsorption method was found to be 74 sq.m./gm. The predominant pore-size in the catalyst, as determined by the method of Cranston and Inkley (1957) was 86 Å (radius). Prior to Kinetics study, the catalyst was tested for activity by actual test runs and the optimum conditions for the maximum activity was determined by varying the temperature, gas composition and space velocity (unpublished results of authors). The catalyst was found to exhibit highest activity at lower temperature (80°C to 90°C). On prolonged use, the activity was found to decline but it could be regenerated to full activity by heating in air at 125°C .

RESULTS AND DISCUSSION

To arrive at meaningful kinetic data it is essential to carry out reactions under conditions where diffusional resistance is negligible. The method of Corrigan (1955) was followed to investigate the diffusion characteristics of the catalyst.

It was observed that with catalyst of particle size -6 to $+14$ mesh B.S.S., the temperature ranging from 30°C to 80°C , the rate of reaction (conversion per minute per volume of the catalyst) did not change with further increase in space velocity

beyond 1500. All kinetics experiments were therefore carried out beyond this space velocity. At 20°C, the threshold value of space velocity was so low as to be almost negligible. The orders of reaction with respect to either of the reactants, namely, CO and O₂ were determined by the variation in the ratio of reactants (Ostwald's method). According to this, the rate of reaction is measured by greatly changing the concentration of reactants, one at a time and observing the change in the rate of reaction over a short period of time i.e., a period in which the change in composition is not more than 10 per cent. From rate measurements at two different concentrations of one of the reactants, the order of reaction with respect to the reactant may be computed. The order of reaction with respect to carbon monoxide was found to be 1 in the temperature ranging from 20°C to 80°C, whereas for oxygen it was 0.6 at 20°C and 0.5 at 40°C to 80°C.

The rate of catalytic oxidation of carbon monoxide was determined as a function of partial pressure of carbon monoxide and oxygen at 20°C, 40°C and 60°C. The results of 20°C are shown in Figs. 1 and 2.

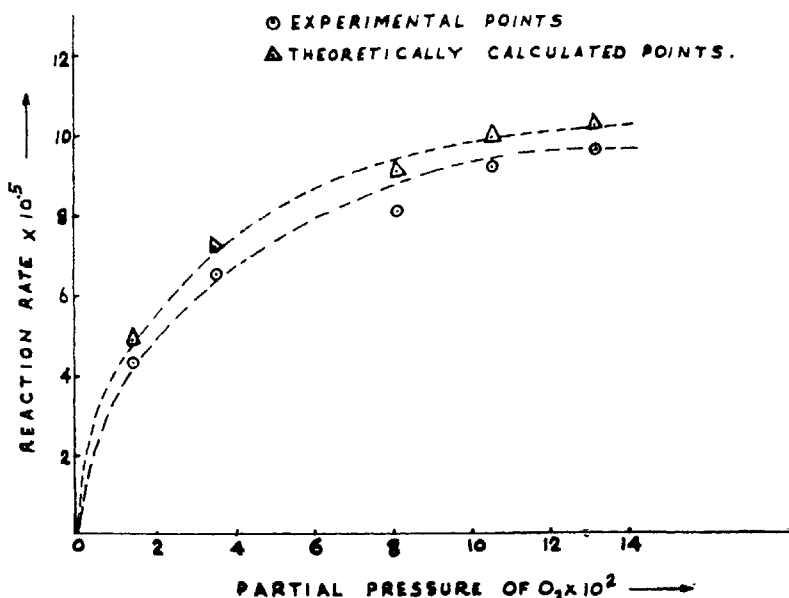
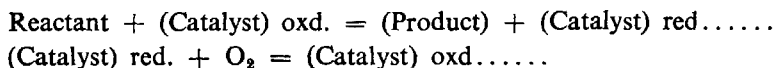


FIG. 1. Effect of partial pressure of oxygen on reaction rate at 20°C.

The kinetic data were examined from different possible mechanisms of reaction and ultimately the rate expression based on a scheme originally proposed by Mars and Van Krevelen (1954) and subsequently applied by Bhattacharyya *et al.* (1967) was found to represent experimental data with a high degree of accuracy. The kinetics model proposed by Mars and Van Krevelen is based on the following assumptions :



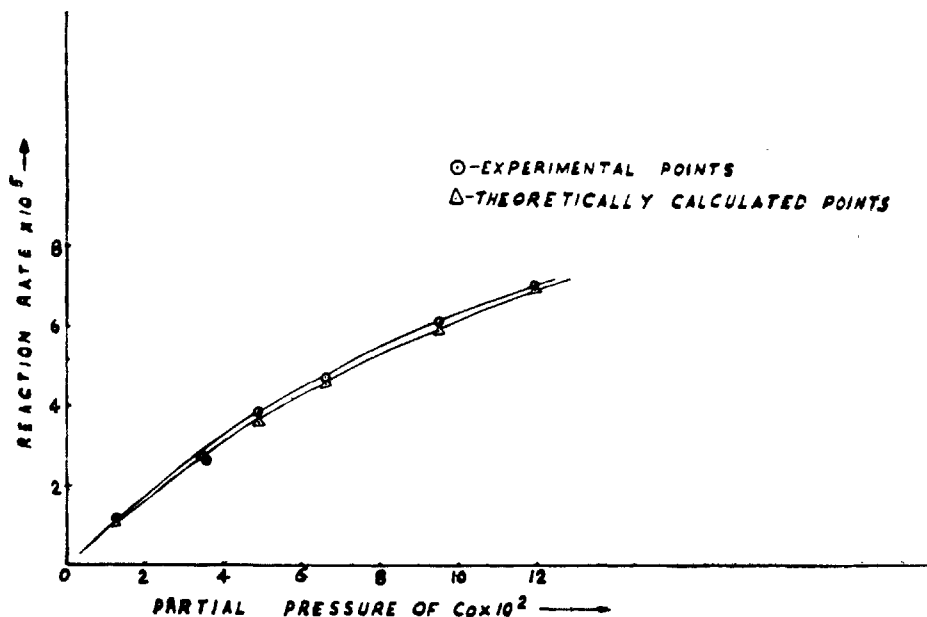
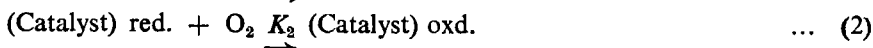
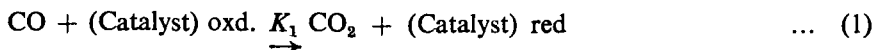


FIG. 2. Effect of partial pressure of CO on reaction rate at 20°C.

The rate expression was derived on the assumption that heterogeneous oxidation of carbon monoxide proceeds through two successive stages, namely, reduction of catalyst surface by carbon monoxide with the formation of carbon dioxide followed by reoxidation of reduced surface by gaseous oxygen. Thus, a steady state is assumed to be attained between the two steps.



The general form of rate expression for reaction (1) is

$$\frac{-dp_{\text{CO}}}{dt} = K_1 p_{\text{CO}}^a \theta \quad \dots (3)$$

where θ is the fraction of surface covered by oxygen.

The rate expression for reaction (2) may be represented as

$$\frac{-dp_{\text{CO}_2}}{dt} = K_2 p_{\text{O}_2}^b (1-\theta) \quad \dots (4)$$

Under steady state

$$\alpha \left(\frac{dp_{\text{CO}}}{dt} \right) = \frac{dp_{\text{O}_2}}{dt} \quad \dots (5)$$

where α is the number of molecules of oxygen required for oxidising one molecule of CO.

From equation (3), (4) & (5)

$$\alpha K_1 p_{\text{CO}}^a = K_2 p_{\text{O}_2}^b (1-\theta)$$

$$\text{or, } \theta = \frac{K_2 p_{O_2}^b}{K_2 p_{O_2}^b + \alpha K_1 p_{CO}^a} \quad \dots (6)$$

Substituting the value of θ in equation (3)

$$\gamma = \frac{K_1 K_2 p_{CO}^a p_{O_2}^b}{K_2 p_{O_2}^b + \alpha K_1 p_{CO}^a} \quad \dots (7)$$

$$= \frac{1}{\frac{1}{K_1 p_{CO}^a} + \frac{\alpha}{K_2 p_{O_2}^b}} \quad \dots (8)$$

By putting appropriate experimental values of a and b which stand for orders of reaction with respect to CO and O_2 , eqns. (7) and (8) were examined for the accuracy with which they represent kinetic data.

At 20°C, the experimental values of a and b are 1 and 0.6 respectively. Equation (8) may be rewritten as

$$\frac{1}{\gamma} = \frac{1}{K_1 p_{CO}} + \frac{\alpha}{K_2 p_{O_2}^{0.6}} \quad \dots (9)$$

At constant $p_{O_2}^{0.6}$

$$\left(\frac{1}{\gamma}\right) p_{O_2}^{0.6} = A + \frac{1}{K_1 p_{CO}} \quad \dots (10)$$

and at constant p_{CO}

$$\left(\frac{1}{\gamma}\right) p_{CO} = A_1 + \frac{\alpha}{K_2 p_{O_2}^{0.6}} \quad \dots (11)$$

where

$$A = \frac{\alpha}{K_2 (p_{O_2}^{0.6})_{\text{Const.}}} \quad \text{and} \quad A_1 = \frac{1}{K_1 (p_{CO})_{\text{Const.}}}$$

According to equations (10) and (11), the plots of $(1/\gamma) p_{O_2}^{0.6}$ against $1/p_{CO}$ and $(1/\gamma) p_{CO}$ against $1/p_{O_2}^{0.6}$ should be linear as shown in Figs. 3 and 4. This demonstrates the validity of the rate equation (9) as well as corroborates the experimental values of reaction order. The values of rate constants K_1 and K_2 were calculated from the intercept of straight lines (Figs. 3 and 4) assuming $\alpha = 0.5$. Theoretical rates were then calculated from the above values of K_1 and K_2 and equation (9). The excellent agreement between theoretical and experimental rate

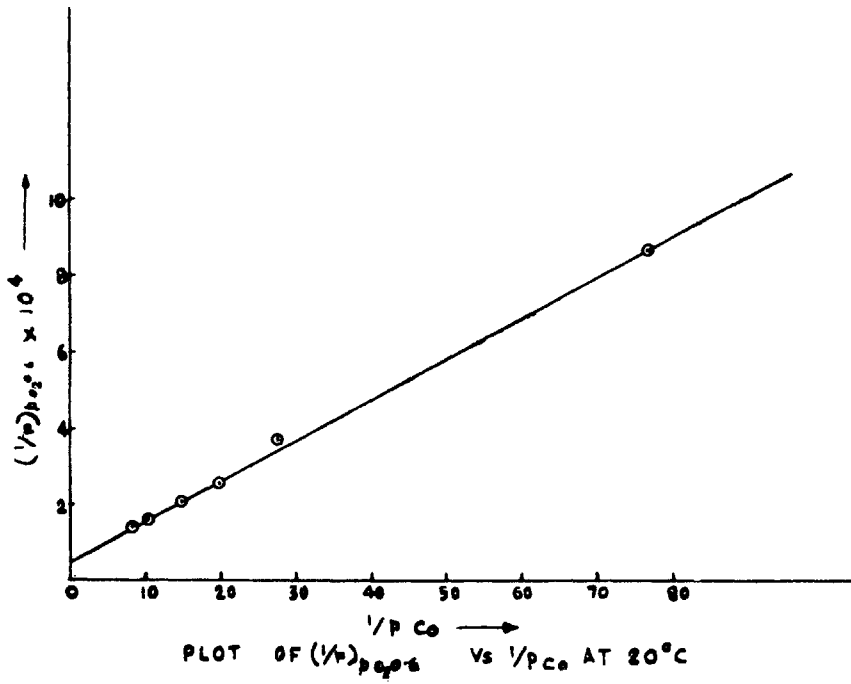


FIG. 3.

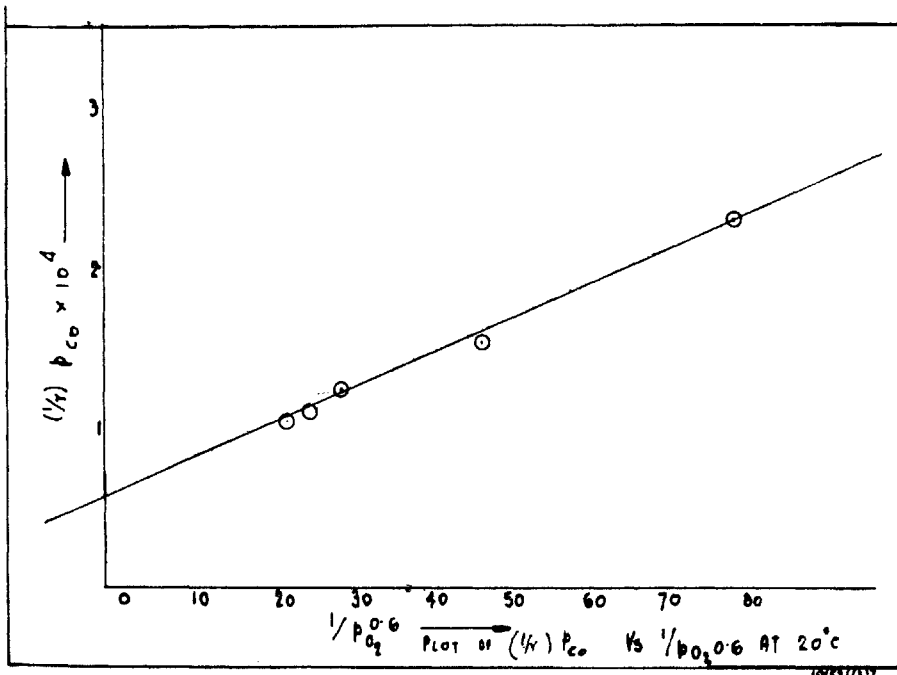


FIG. 4.

TABLE I

Specific rate constants	20°C	40°C	60°C	Activation Energies (kcal/mole)
K_1	0.086×10^{-2}	1.32×10^{-2}	8.25×10^{-2}	9.47
K_2	0.31×10^{-2}	3.95×10^{-2}	20.18×10^{-2}	8.82

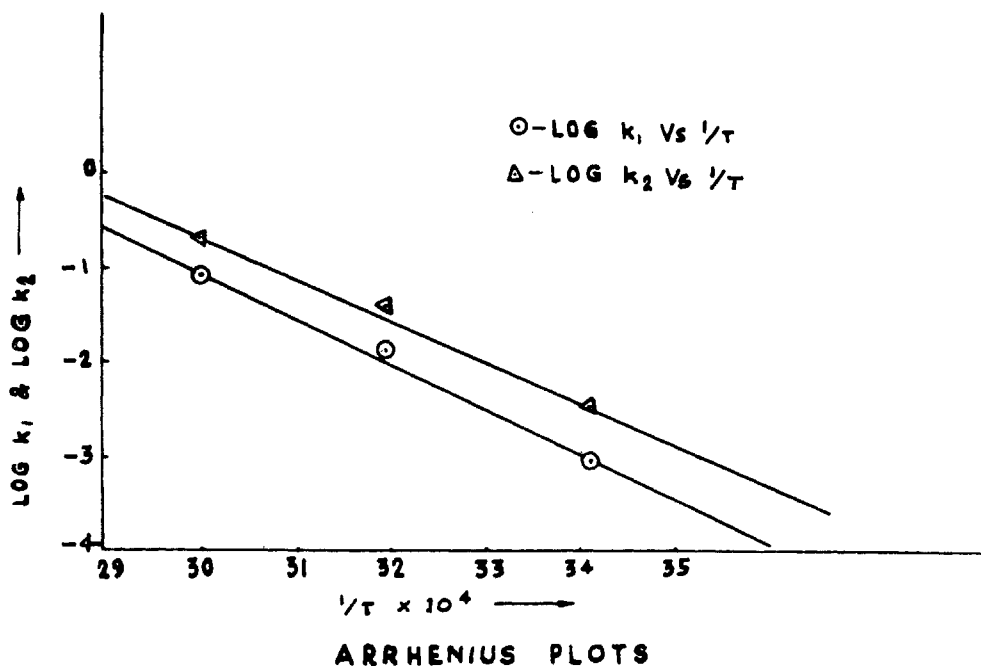


FIG. 5.

curves as shown in Figs. 1 and 2 once again demonstrates the validity of rate expressions.

The kinetics data at 40°C and 60°C were treated in a similar way and rate constants were calculated at 40°C and 60°C.

The values of rate constants K_1 and K_2 as well as energies of activation for the reaction steps (1) and (2) are presented in Table I. The activation energies were calculated from the Arrhenius plots as shown in Fig. 5.

Satisfactory representation of kinetic data by rate equation does not necessarily prove the validity of the assumptions on which the rate equation is based. In the present case, for example, same rate expression may be derived from modified Hinshelwood mechanism, according to which chemisorbed oxygen reacts with CO in the gas phase and the rate of removal of oxygen by the reaction is equal to the rate of adsorption of oxygen (Hinshelwood 1940). It is thus evident that from kinetics study alone it is not possible to settle the actual steps involved in the reaction. Attempts have been made in the past to elucidate the mechanism of reaction by adsorption

measurements. It has been demonstrated that considerable amount of oxygen is adsorbed on active catalysts after it had adsorbed CO and this is in spite of the fact that very little oxygen is adsorbed by the same catalyst prior to CO adsorption (Ward 1947). Further, the volume of oxygen adsorbed is exactly half of the presorbed CO. This apparently indicates that the reaction proceeds through surface reaction between the adsorbed species of reactants. A rate equation based on the above mechanism is however completely at variance with the kinetics data as has been shown by Bhattacharyya (1967). Whatever might be the precise mechanism, from kinetics studies it appears that two major stages are involved in the process and none of them preferentially affects rate of reaction as is evident from the same order of values for the activation energies (Table I).

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