

The Oxidation of Carbon Monoxide on Supported Platinum

A STUDY OF HONEYCOMB CATALYST REACTION KINETICS

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Reliable kinetic rate data have not previously been available for the oxidation of carbon monoxide on platinum catalysts used in the control of automobile exhaust emissions. This paper discusses results of studies using an isothermal differential catalyst bed and confirms that mass transfer and pore diffusion did not control the reaction rate, so that the observed kinetics represent the true surface reaction rates.

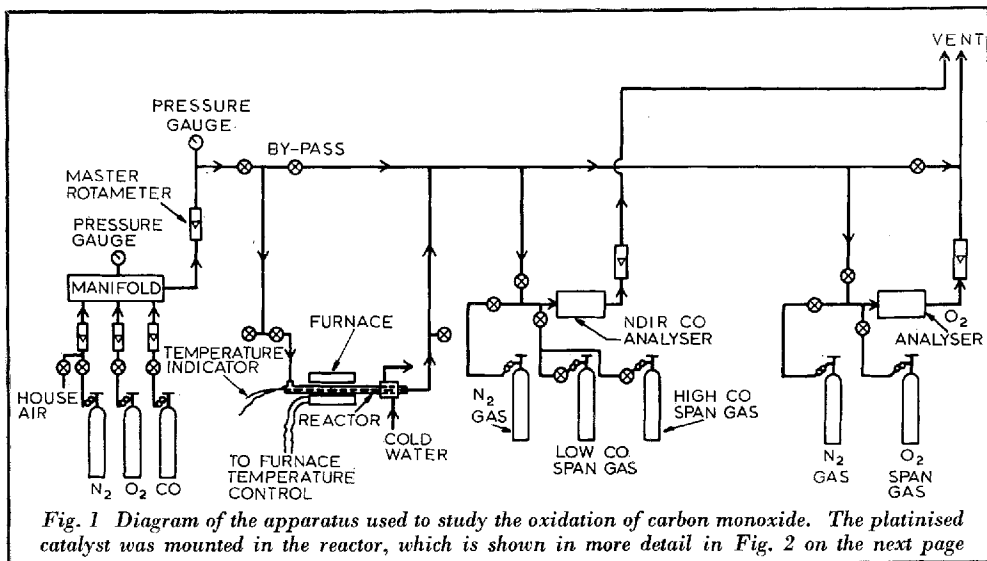
A number of investigations on oxidation of carbon monoxide over platinum catalyst have been reported (1-8). The conclusions of various investigators regarding the kinetics of this reaction are rather conflicting. According to one group both carbon monoxide and oxygen must be adsorbed on the catalyst surface to form the reaction product. On the other hand, others contend that only one reactant need be adsorbed on the catalyst while the other must originate from the gas phase. There is general agreement, however, that the oxidation mechanism changes with temperature. At low temperatures the reaction is inhibited by carbon monoxide (1). At higher temperatures the reaction is limited largely by bulk gas-phase diffusion (1,3,5). The temperature at which this occurs lies between 572°F (300°C) (3) and 960°F (545°C) (1).

The purpose of this investigation was to obtain a reliable kinetic rate expression for carbon monoxide oxidation on a platinum catalyst in an isothermal differential bed over the concentration ranges prevailing in automobile exhaust gases, and to demonstrate the validity of this rate expression for a non-

isothermal reactor. In this paper only the first phase will be discussed. The second phase involving a non-isothermal bed will be reported later.

A schematic diagram of the experimental apparatus is shown in Fig. 1. The flow rates of nitrogen carrier gas, oxygen and diluted carbon monoxide were measured with calibrated flowmeters. The gases were passed through a stainless steel manifold used as a mixing chamber and then through a master flowmeter to measure the total flow rate. The composition of the feed gas was determined by passing the gas mixture through carbon monoxide and oxygen analysers. Once the composition was determined, the gas was passed through the catalyst bed placed in a quartz tube reactor. At the steady state the extent of conversion was measured. A Beckman model IR-215 non-dispersive infrared analyser was used to analyse carbon monoxide. Oxygen was measured by a Beckman Model F3 paramagnetic analyser.

Platinised honeycomb having the characteristics listed in Table I was used for this study. It was difficult to prepare test samples of the honeycomb with a round cross-section



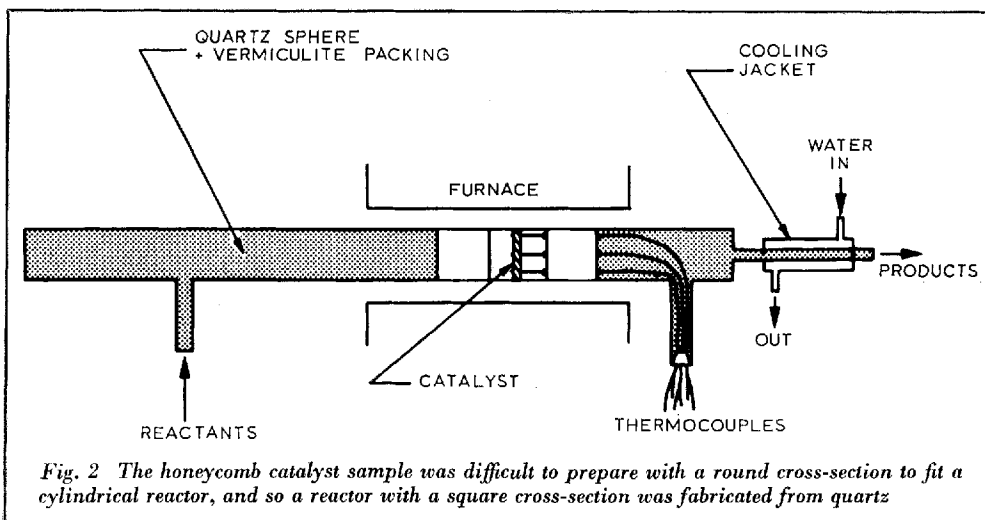
such that the sample would fit in a round tube snugly enough to avoid appreciable gas by-passing near the walls. Therefore, a square quartz tube reactor, shown schematically in Fig. 2, was used. The pre-heating and after-cooling sections were filled with an inert packing of pyrex beads (3 mm diameter) and vermiculite. This packing was found to be inert in a previous study. A Lindberg

furnace was used to preheat the gas mixture and to maintain the catalyst section at the desired temperature level.

The catalyst bed was a thin slice ($\frac{1}{8}$ in deep) of platinised honeycomb. Two inert support cubes of honeycomb channel were used to provide calming zones before and after the catalyst section. Temperatures at several locations on both faces of the catalyst were measured to ascertain that essentially isothermal conditions were obtained. Since the chemical reaction takes place on the surface of the catalyst, the thermocouples were cemented to the surface. The cement was found to be inert for carbon monoxide oxidation. Chromel-Alumel thermocouples were used. Three thermocouples were used on each face: one at the centre, one at an edge and one at a corner (see Fig. 3). Isothermal conditions were maintained in the reactor both axially and radially within $\pm 3^\circ\text{F}$.

A flow rate was established such that film diffusion was not rate limiting. The initial concentration of carbon monoxide was varied from 0.2 to 2.0 per cent while that of oxygen was varied from 0.13 to 2.1 per cent. Several possible combinations of carbon monoxide and oxygen concentrations were studied. These correspond to rich, lean and stoichiometric conditions. The lowest temperature

Weight	0.0026 lb
Dimension	$\frac{1}{16} \times \frac{1}{16} \times \frac{1}{8}$ in
Pt content	0.14% (by weight)
Support material	Mullite coated with alumina
Support type	Hexagonal channels
Nominal channel size	$\frac{1}{8}$ in
Hydraulic mean diameter of channel	0.133 in
Bulk density	40.8 lb/ft ³
Void volume	55%
Est. geometric surface	300 ft ² /ft ³
BET surface area	12 m ² /g



studied for each set of carbon monoxide and oxygen concentrations corresponded to that temperature which resulted in the lowest detectable conversion. The upper temperature was limited to that which allowed maintenance of the isothermicity of the bed. Temperatures higher than that yielded higher conversions, and rendered the bed non-isothermal because of high heat of reaction. The range of temperature studied was 460 to 800°F.

Experimental data obtained with the isothermal differential reactor are given in Table II. This includes only those data which have a maximum conversion of carbon monoxide up to 10 per cent so that they could be treated as differential bed data for the analysis. The complete set of experimental data is given elsewhere (9).

The rate of carbon monoxide oxidation was calculated from the design equation,

$$r = \frac{\Delta X}{\Delta(W/F)} \quad (1)$$

where r is the rate of reaction, ΔX is the conversion, W is the catalyst weight and F is the molal flow rate of carbon monoxide. Calculations similar to those made by Potter and Baron (10) indicated that mass transfer effects were negligible. Estimated values of Thiele's modulus indicated that pore diffusion hindrance was also negligible.

The correlation of the reaction rate data was attempted with a simple power-law rate model and a number of reaction rate expressions based on Langmuir-Hinshelwood's mechanism. The model parameters were estimated using a non-linear least squares technique suggested by Levenberg, Meiron and Fraser (11, 12, 13).

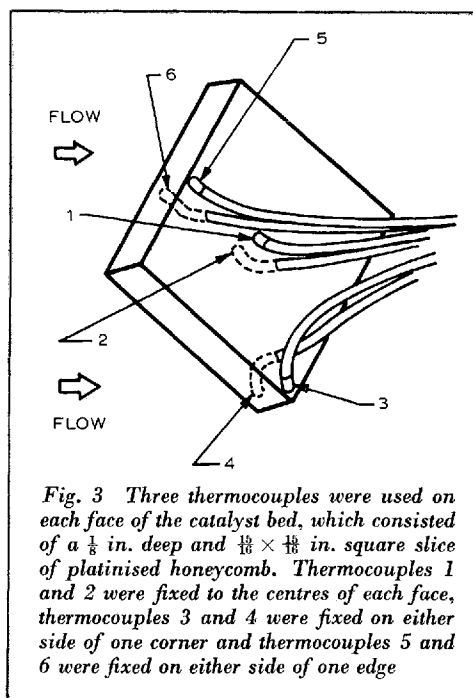


Table II
Experimental Results for Catalytic Oxidation of Carbon Monoxide
on Platinum Catalyst—Isothermal Differential Bed Data

Run	Flow Rate SCFH	Feed Composition		Total Conversion %	Reactor Pressure atm	Bed Temperature °F
		%CO	%O ₂			
17	35.8	0.40	1.0	5.7	1.07	502.1
19	35.8	0.41	1.0	8.4	1.07	523.5
74	35.7	1.04	1.97	3.4	1.08	504.3
75	35.7	1.04	1.97	4.4	1.08	524.4
85	44.9	0.21	0.50	6.8	1.13	494.8
79	43.9	1.02	2.12	6.4	1.11	548.6
89	44.2	1.02	2.0	7.4	1.13	555.3
90	44.2	1.02	2.1	4.4	1.13	531.7
25	35.7	0.21	0.53	8.7	1.08	481.6
26	35.7	0.22	0.55	7.0	1.08	479.0
32	35.7	0.20	0.51	5.5	1.08	461.4
7	26.8	0.40	0.21	7.2	1.05	581.2
33	26.7	0.40	0.21	5.2	1.04	577.2
57	35.7	1.98	1.0	3.3	1.08	620.1
58	35.7	1.98	1.0	4.6	1.08	634.9
13	35.6	0.39	0.2	7.6	1.07	601.3
92	35.9	0.39	0.2	7.1	1.09	594.2
67	15.0	1.0	0.13	3.5	1.01	653.3
68	15.0	1.0	0.13	6.5	1.01	714.0
64	15.0	2.0	0.21	5.0	1.01	719.1
65	15.0	2.0	0.21	5.7	1.01	753.2
66	15.0	2.0	0.21	7.5	1.01	790.0
54	26.8	2.0	0.22	3.0	1.05	708.5
55	26.8	2.0	0.22	5.0	1.05	764.5
56	26.8	2.0	0.24	6.5	1.05	804.0

Power-law Model

All the data were correlated by the rate expression

$$r = 2.25 \times 10^5 e^{-28850/RT} \frac{P_{CO}}{(P_{O_2})^{0.5}} \text{ moles CO/h.lb cat.} \quad (2)$$

where the standard deviation is 1.87×10^{-3} moles CO/h.lb cat. The orders of reaction of 1.0 and -0.5 with respect to O₂ and CO respectively are in agreement with other in-

vestigators (8). An Arrhenius plot is shown in Fig. 4. A graphical comparison of predicted and observed conversion is shown in Fig. 5.

It has been postulated that the CO inhibition effect on the reaction rate is due to fast and strong adsorption of carbon monoxide that inhibits the oxygen adsorption. Several possible rate controlling steps could be postulated. The data of the present investigation

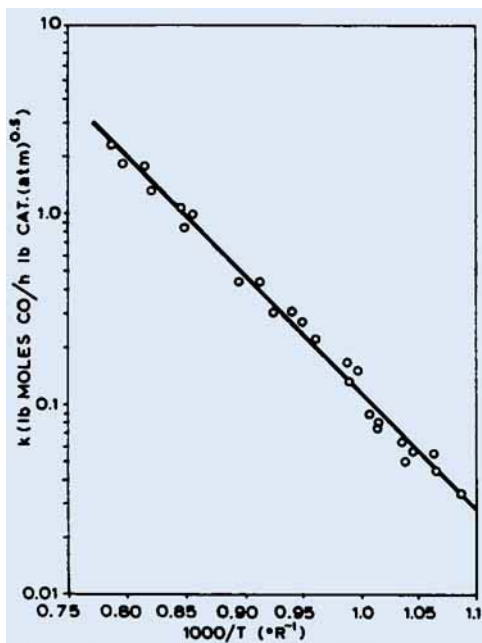


Fig. 4 Arrhenius plot for the power-law rate model of carbon monoxide oxidation on the platinised honeycomb catalyst

is not sufficient to specify indisputably a particular reaction mechanism. However, the same argument of fast and strong adsorption of carbon monoxide could be invoked.

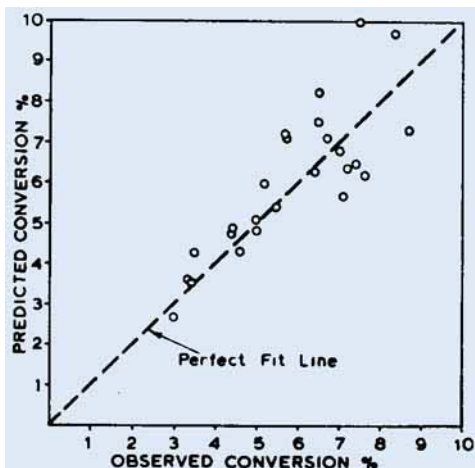


Fig. 5 Observed conversions plotted against predicted conversions for the power-law rate model of carbon monoxide oxidation on the platinised honeycomb catalyst

The power-law model, as shown in equation (2) has a limitation because of the rate being inversely proportional to the 0.5 power of partial pressure of carbon monoxide. This predicts an infinite reaction rate as the partial pressure of carbon monoxide approaches zero. Intuitively, one would expect that the reaction rate becomes zero as the partial pressure of carbon monoxide approaches zero. Therefore, the extrapolation of the model beyond the range of experimental conditions may be erroneous.

Langmuir-Hinshelwood Model

Attempts were also made to fit the data to Langmuir-Hinshelwood models, each of which is based on some plausible mechanism of reaction. Out of several possible models considered, a satisfactory correlation was achieved only by the rate equation shown in equation (3).

$$r = \frac{kK_{CO}K_{O_2}P_{CO}P_{O_2}}{(1 + K_{CO}P_{CO} + K_{O_2}P_{O_2})^2} \text{ moles CO/h.lb cat.} \quad (3)$$

This model is generally referred to as the dual site model. Estimated parameters are:

$$k = 2.31 \times 10^9 e^{-45400/RT} \text{ moles CO/h.lb cat.}$$

$$K_{CO} = 2.16 e^{10600/RT} \text{ atm}^{-1}$$

$$K_{O_2} = 1.30 \times 10^{-4} e^{24830/RT} \text{ atm}^{-1}$$

where the standard deviation is 1.78×10^{-3} moles CO/h.lb cat.

The logarithms of these constants were plotted against reciprocal absolute temperatures in Fig. 6. Fig. 7 compares calculated and experimental conversion.

This model does not have the limitation as stated about the power-law model. The denominator remains a finite quantity as the partial pressure of CO approaches zero.

The derivation of the dual-site rate equation has been given by Corrigan (14) and others, based on a model of surface reaction between two different adsorbed reactants on adjacent sites. However, it should be emphasised here that, in this study, engineering analysis of the data has been made and rate equation (3) should be considered an empirical rate model.

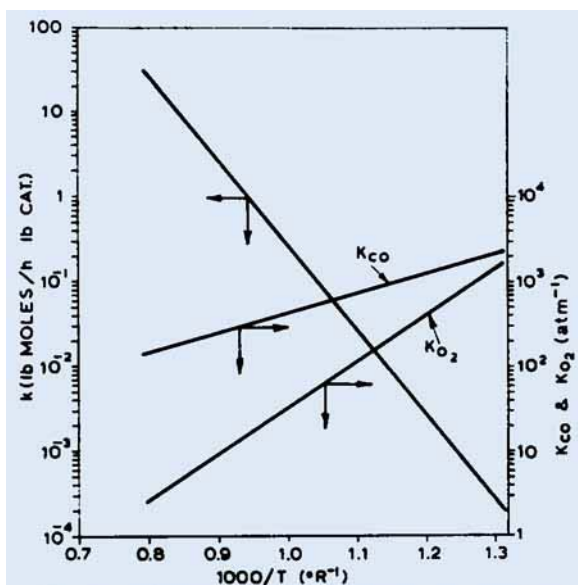


Fig. 6 Arrhenius plot for the dual-site rate model of carbon monoxide oxidation on platinumised honeycomb catalyst

As shown in Figs. 5 and 7, the agreement between experiments and calculations for both power-law and dual-site models is reasonably good, indicating satisfactory correlation of the data. The use of these rate models was made to predict the behaviour of a non-isothermal reactor. The power-law

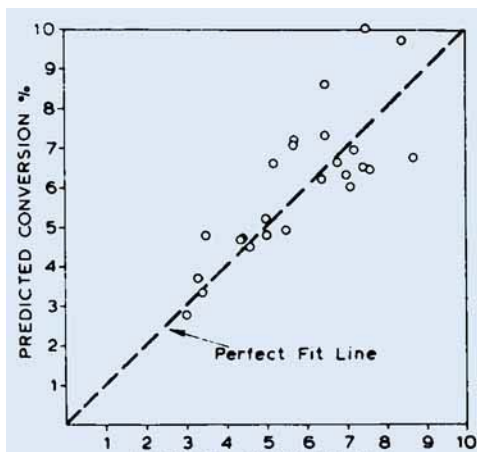


Fig. 7 Observed conversions plotted against predicted conversions for the dual-site rate model of carbon monoxide oxidation on the platinumised honeycomb catalyst

model failed to predict the behaviour of the non-isothermal bed under conditions of low initial carbon monoxide concentration and high conversion. The temperature and concentration profiles in the non-isothermal bed are predicted satisfactorily by the dual-site rate model. These results will be reported in detail in a later paper.

Conclusions

The experimental results and calculations show that for the conditions of the experiments and type of catalyst used in this work the bulk phase mass transfer and pore diffusion resistance do not control the rate of catalytic oxidation of carbon monoxide on platinum. Therefore the observed kinetics represent the true surface reaction

rates. In agreement with other investigators the oxidation rate showed an inhibition effect due to carbon monoxide.

The differential isothermal bed data could be correlated equally well by a simple power-law model and by a Langmuir-Hinshelwood dual-site model. The orders of the reaction in the power-law model are $+1.0$ with respect to O_2 and -0.5 to CO . The power-law model has a limitation at low partial pressure of carbon monoxide (p_{CO}) and high conversion as the rate becomes infinite for p_{CO} approaching zero. The dual-site model does not have this limitation.

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A New Mining Area for Rustenburg

For many years now Rustenburg Platinum Mines has been the largest producer of platinum and its allied metals in the world and successive stages of expansion have been reported here from time to time. Further moves to increase capacity to over 1,500,000 ounces of platinum a year are now under way with the opening of a new mining area with an additional capacity initially of 225,000 ounces a year. The two mining areas at present being exploited are at Rustenburg itself and at the Union Section about 100 kilometres to the north, where altogether

14 vertical shafts are in operation as well as a great number of incline winzes. The new mine, to be known as the Amandelbult Section, lies some 30 kilometres to the north-east of the Union Section. At the present time three vertical shafts are being sunk to extract ore from the deeper areas as well as 21 incline winzes, one of which is illustrated below, designed to work the shallower parts of the deposit. The treatment and refining plants of Matthey Rustenburg Refiners are, of course, being expanded to cope with the increased output from the mines.

