

Oxidation of CO on Polycrystalline Platinum

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The catalytic oxidation of CO on polycrystalline platinum at low temperature ($T < 500\text{K}$) and low oxygen pressure ($P_{\text{O}_2} = 10^{-5}\text{ Pa}$) has been studied. The oxidation is found to occur via the surface reaction between chemisorbed O and CO species (Langmuir-Hinshelwood type-II mechanism, LH_{II}). A rate law with the exponential term depending on the coverage of CO is suggested. The kinetic parameters, namely $E_{\text{LH}_{\text{II}}}$ and $\alpha_{\text{CO}} = \mu_{\text{CO-CO}} + \mu_{\text{CO-O}}$, the former being the activation energy of the surface reaction and the latter indicating the extent of the interaction of the chemisorbed species, come out to be 34.7 kJmol^{-1} and 17.6 kJmol^{-1} respectively. A mathematical model simulating the overall CO oxidation (according to both LH_I and LH_{II} schemes) has also been suggested and tested on the basis of the results gathered in this study.

There is no general agreement on the kinetics and mechanism of catalytic oxidation of CO on platinum though it is one of the simplest type of reactions. Two Langmuir-Hinshelwood schemes, LH_I and LH_{II} , have recently been proposed¹. The LH_I -type scheme¹ envisages the interaction of CO adsorbed on the top of chemisorbed oxygen atoms with oxygen species, resulting in the desorption of CO_2 . The activation energy of this reaction path at zero surface coverage has been found to be zero¹. The LH_{II} -type mechanism envisages the interaction of both chemisorbed CO and O species.²⁻⁵ The LH_{II} mechanism seems to prevail under the conditions of low temperature and high CO/O_2 partial pressure ratios; the latter points to the fact that pre-adsorbed oxygen atoms (species) readily react with weakly held precursor CO molecules^{1,6}, while the reaction between adsorbed CO and gaseous oxygen is slow.

The purpose of the present work is to investigate the kinetic aspects of the oxidation of CO on polycrystalline platinum under LH_{II} conditions. A mathematical model which simulates the system and also helps in the calculation of the kinetic parameters of similar reactions with adsorbate-adsorbate interactions deviating the adsorption isotherms from the simple Langmuir type is also briefly discussed.

Materials and Methods

Details of the ultra-high vacuum system, the sample and the techniques used in this work were reported previously⁶. The temperature range used in this work was 300-500K and maintained with an accuracy of $\pm 0.5\text{K}$. The cleanliness of the polycrystalline platinum sample was tested by comparing the flash

desorption spectra of CO and O_2 with these from surfaces which were clean according to Auger spectra⁷. The oxygen coverages were determined using the pressure jump method in which the amount of CO_2 produced from the reaction of CO with the surface oxygen gave the coverage of the latter. The amount of CO_2 produced was normalized to the amount desorbed from the oxygen saturated surface. The flash desorption method was used to measure the CO coverage under steady state conditions. The values of the CO and oxygen coverages (θ_{CO} , θ_{O}) were found to be internally consistent since $\theta_{\text{CO}} + \theta_{\text{O}}$ never exceeded unity. Prior to the kinetic measurements the substrate was exposed to 10^{-4} Pa of oxygen and heated to 1000K for 15 min to ensure reproducibility of the results. Nonreactive oxygen remaining on the surface amounted to nearly 10% of the complete coverage.

Results

Figure 1 presents the variations in the rate of formation of CO_2 at a constant oxygen pressure of 10^{-5} Pa with respect to CO pressure at different temperatures. Asymptotic decrease in the rate with increasing CO pressure has been observed. Figure 1 also presents coverages of CO under working conditions. The changes in the coverage of oxygen with respect to CO pressure in the temperature range of 453 to 498K are presented in Fig. 2. These results form the basis of the plots shown in Figs 3 and 4.

Discussion

In our previous work¹ by assuming that only CO surface diffusion occurred we showed that the rate law (1)

$$R_{LH_{II}} = K_{LH_{II}} \theta_{CO} \theta_O \exp - \left[\frac{E_{LH_{II}} + (\mu_{CO-CO} + \mu_{CO-O}) \theta_{CO} + \mu_{CO-O} \theta_O}{RT} \right] \dots (1)$$

was compatible with the LH_{II} mechanism. In the rate Eq. (1) μ s signify the extent of the average interactions of neighbouring species and θ s are their corresponding coverages. The $\mu_{CO-O} \theta_O$ term can be neglected on account of the low coverage of oxygen under the LH_{II} -type mechanism and Eq. (1) can be simplified to Eq. (2)

$$R_{LH_{II}} = K_{LH_{II}} \theta_{CO} \theta_O \exp \left(- \frac{E_{LH_{II}} + \alpha_{CO} \theta_{CO}}{RT} \right) \dots (2)$$

where $\alpha_{CO} = \mu_{CO-CO} + \mu_{CO-O}$. The logarithmic form of Eq. (2) is:

$$\ln \left(\frac{R_{LH_{II}}}{\theta_{CO} \theta_O} \right) = \ln(K_{LH_{II}}) - \frac{E_{LH_{II}}}{RT} - \frac{\alpha_{CO} \theta_{CO}}{RT} \dots (3)$$

The plots of $\ln(R_{LH_{II}}/\theta_{CO} \theta_O)$ versus θ_{CO} at various temperatures are linear with slopes of $17 \pm 2 \text{ kJmol}^{-1}$ (Fig. 3). These linear plots indicate the validity of Eq. (2) or (3). The plot of $\ln(R_{LH_{II}}/\theta_{CO} \theta_O) + \alpha_{CO} \theta_{CO}/RT$ versus $1/T$ (Fig. 4) is also linear, the slope and intercept of which give the values of $E_{LH_{II}}$ and $K_{LH_{II}}$ as $34 \pm 2 \text{ kJmol}^{-1}$ and $(2.2 \pm 0.5) \times 10^4 \text{ mol site}^{-1} \text{s}^{-1}$ respectively.

Bonzel and Burton⁸ using a CO presaturated surface and a transient regime at 410K observed a transient curve compatible with an LH_{II} -type

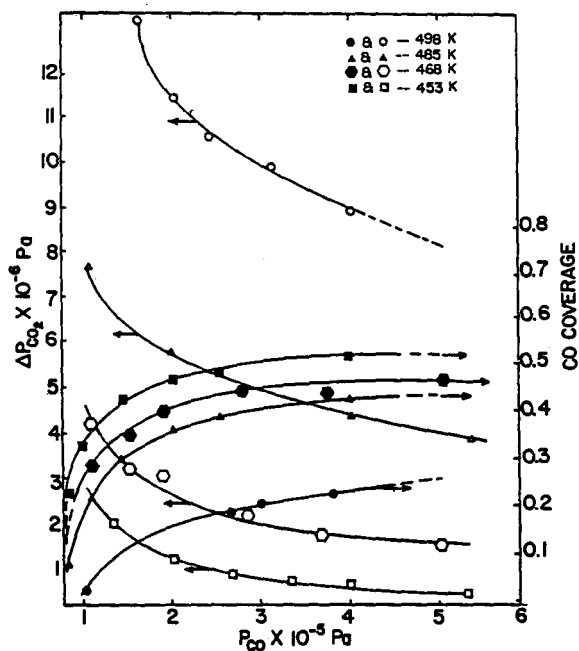


Fig. 1—Plots of steady state CO_2 production rates (open symbols) and CO coverages (closed symbols) as a function of CO pressure for a fixed O_2 pressure of 10^{-5} Pa at different temperatures.

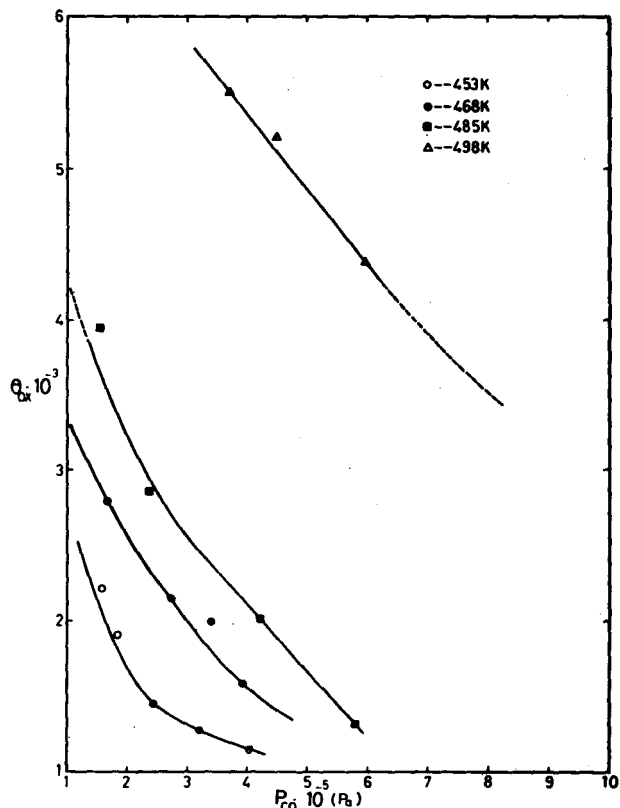


Fig. 2—Oxygen coverages as a function of CO pressure at different temperatures for a fixed O_2 pressure of 10^{-5} Pa and $P_{\text{CO}} > P_{\text{O}_2}$.

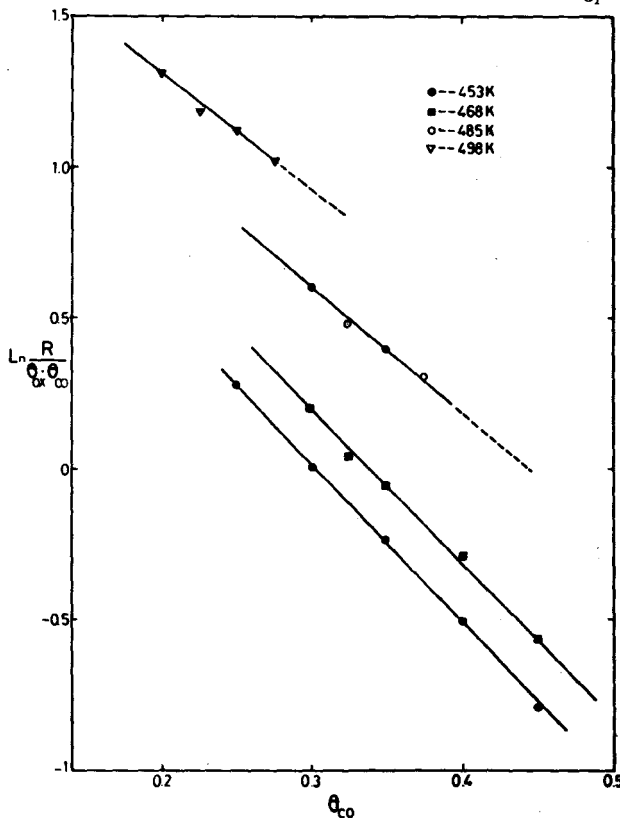


Fig. 3— CO_2 production rate (normalized to unit O coverage and unit CO coverage) as a function of CO coverage at different temperatures.

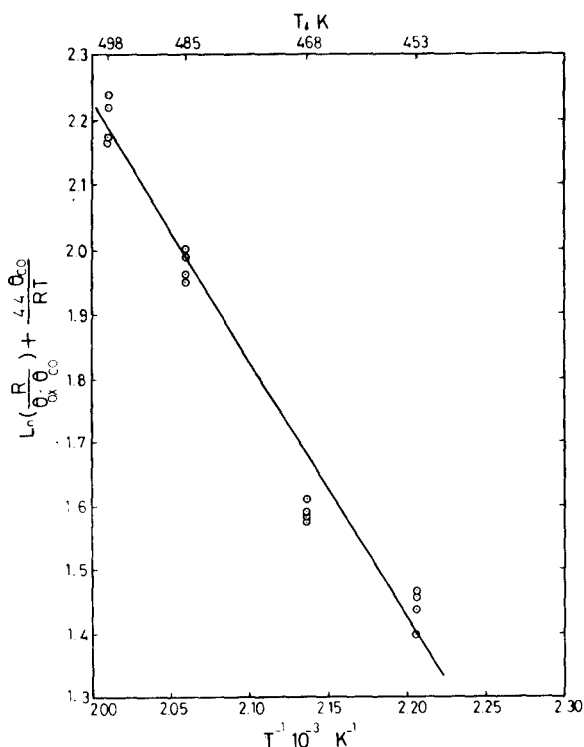


Fig. 4—Plots of $\ln(R_{LHII}/\theta_{CO}\theta_O) + 4.4 \theta_{CO}/RT$ as a function of $1/T$.

mechanism and found the activation energy of 33.02 kJmol^{-1} . The E_{LHII} obtained by us ($34 \pm 2 \text{ kJmol}^{-1}$) is in fair agreement with this value. Our previous results confirm that under the present experimental conditions where the temperature is low and the CO/O_2 pressure ratio is high (the necessary conditions for an LH-type scheme to prevail), the CO coverage approaches the value it assumes in the absence of oxygen (the isotherm value) and the oxygen coverage is nearly two orders of magnitude lower. The activation energy in an LH_{II} -type scheme is utilized for the surface diffusion of the chemisorbed species⁹ while the activation energy of the surface recombination of $\text{CO}-\text{O}$ (or reaction) and the activation energy of the desorption of CO_2 are negligible. In fact, calculations based on Eq. (4) and $\theta_{\text{CO}} = 0.4$ gave an activation energy of nearly 41.8 kJmol^{-1} compared to the value of 42.2 kJmol^{-1} reported for the surface diffusion of CO on platinum⁹. The values of the activation energy derived from the results presented in Fig. 1 and using simple Arrhenius criteria are in the range of 96.1 – 146.3 kJmol^{-1} and are strongly temperature and CO coverage dependent. This indirectly signifies the validity of the derivations made on the basis of LH_{II} -type scheme where the effects of coverage and nearest neighbour interactions have explicitly been included. The latter factor appears as α_{CO} in the calculations and represents the strength of the interactions of $\text{CO}-\text{CO}$ and $\text{CO}-\text{O}$ couples.

The overall reaction can be expressed in terms of a combination of LH_I and LH_{II} -type reactions. Both the types of reactions consume chemisorbed oxygen atoms (in LH_I scheme the oxidation goes via the interaction of CO molecules adsorbed on the top of surface oxygen atoms with their sites⁶). Under the condition of $P_{\text{O}_2} > P_{\text{CO}}$ the oxygen coverage is high⁶ and with increasing P_{O_2} no further change⁶ in the rate is observed. Although there is an increase in oxygen coverage as has previously been shown^{1,6} the reactivity of the absorbed oxygen falls. Using $\mu_{\text{O}-\text{O}} = 8.86 \text{ kJmol}^{-1}$ and $\alpha_{\text{CO}} = 17.56 \text{ kJmol}^{-1}$ in the rate equation results in an exponential term which shows a similar effect at $P_{\text{O}_2} < P_{\text{CO}}$, namely when the LH_{II} -type scheme dominates. In other words, the probability of the reaction to follow the LH_{II} -path also decreases with increase in reactant coverages. However, under the LH_{II} -scheme conditions the oxygen coverage is very low, and at $T < 540 \text{ K}$ CO accumulates on the surface of the substrate, thereby decreasing the fraction of the unoccupied sites sharply. At the same time, the oxygen coverage also decreases rapidly resulting in substantial decrease in the rate of CO_2 production. Hence, under these conditions the formation of CO_2 is controlled by the rate of formation of oxygen atoms on the surface, the latter increases with increase in the pressure of oxygen provided P_{O_2} is always kept lower than the pressure of CO to prevent transition between two kinetic schemes. Explicit calculations based on the numerical solution of coupled differential equations describing the rate laws for the consumptions of oxygen and CO and formation of CO_2 with the parameters obtained in this and previous works ($E_{\text{LH}} = 34.7$, $\mu_{\text{O}-\text{O}} = 8.36$, $\alpha_{\text{CO}} = 17.56 \text{ kJmol}^{-1}$) have been carried out. The results are presented in Fig. 5 in the form of rates versus P_{CO} plots at a fixed pressure of oxygen. Apart from the loop which probably arises from the inadequacies in the model and has no physical significance, the rising and falling parts are in fair

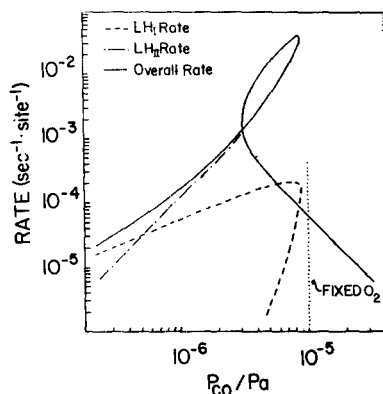


Fig. 5—Computer plot of the CO_2 production rate as a function of CO pressure for a fixed O_2 pressure ($10^{-5.5} \text{ Pa}$) on polycrystalline platinum at 300 K .

agreement with the experimental results⁶. The sudden decrease in the rate which occurs at a critical $P_{\text{CO}}/P_{\text{O}_2}$ ratio indicates changes in both the preexponential and exponential factors and the conversion of the chemisorbed CO species from their reactive states into their largely chemisorbed states. In the critical range of $P_{\text{CO}}/P_{\text{O}_2}$, an increase in P_{CO} inhibits the rate of oxidation in two ways: (i) it increases the rate of conversion of CO into its adsorbed precursor state, which exceeds the rate of its removal via oxidation and causes the accumulation of adsorbed CO molecules; and (ii) it decreases the rate of oxidation as a result of decrease in the oxygen coverage by adsorbed CO species. These two phenomena are complementary and bring about a sharp drop in the total rate of oxidation in a limited interval of $P_{\text{CO}}/P_{\text{O}_2}$ change. It has previously been shown⁶ that higher the temperature the smaller the magnitude of the sharp drop in the rate at a particular $P_{\text{CO}}/P_{\text{O}_2}$ ratio. This in turn suggests that in a particular range of $P_{\text{CO}}/P_{\text{O}_2}$, some kind of ordering occurs in the surface CO phase which is less stable at higher temperatures where the system approaches simple LH-type of behaviour. The approach to the mentioned

range from different boundaries is manifested in different on-set rates and obviously a kind of hysteresis loop. The behaviour has been discussed in detail elsewhere⁶ where it has been suggested that the rates of entering into the ordered metastable regime are different at different pressure ratio limits.

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