

NOTES

The Oxidation of Hydrogen and Carbon Monoxide Mixtures Over Platinum

The oxidation of hydrogen over platinum catalysts is well documented (1-3) and is established as a technique for the determination of the platinum surface area of supported catalysts (4, 5). In addition a good deal of work has been done on the oxidation of carbon monoxide over similar catalysts (6, 7). Studies of the co-adsorption of carbon monoxide and hydrogen (8, 9) and carbon monoxide, hydrogen, and oxygen (10) on platinum group catalysts have also been made, complementing the thorough studies made of each gas individually. Relatively little attention, however, has been given to the oxidation of gaseous mixtures over metal surfaces. It has been shown (11) that a stream of hydrogen at atmospheric pressure may be purged of carbon monoxide impurities ($P_{CO} \leq 2 \text{ kN m}^{-2}$) by the addition of oxygen, in approximately 2:1 (oxygen:carbon monoxide) molar ratio, and oxidation over a platinum-alumina catalyst at 393-433 K. In this reaction it was found that only the oxygen in excess of that required to oxidize the carbon monoxide was consumed by reaction with hydrogen. This result is contrary to that expected on the basis of the behavior of each gas individually. We present here the results of a study of the oxidation of hydrogen and carbon monoxide in low concentrations over a platinum catalyst, under strongly oxidizing conditions.

The catalyst, in the form of thermopure platinum wire (5×10^{-2} mm in diameter),

was wound into an 11-turn coil of pitch 12.5×10^{-2} mm. The coil was pretreated by being heated electrically to 900°C in flowing air for 5 min to remove carbon deposits, and for a further 30 min at 300°C to ensure the reproducible formation of a well-oxidized surface. The isothermal calorimeter technique (12) was used to obtain kinetic data. The rate of reaction is monitored as the change in electrical power required to maintain the catalyst at constant temperature in the presence of reaction at the catalyst surface. The heating current is passed directly through the platinum coil which acts as its own resistance thermometer. With this technique a temperature stability of $\pm 2^\circ$ could easily be achieved. The catalyst was held in a conventional atmospheric pressure flow system previously described (1). All gases, supplied by high-pressure cylinders, were dried and purified by magnesium perchlorate and charcoal filters before they were brought into contact with the catalyst. A correction was made for the thermal conductivity effects of each gas mixture used via a second, catalytically inert, calorimeter consisting of a rhodium/platinum coil encapsulated in alumina.

The temperature dependences of the rates of oxidation of hydrogen (0.5 kN m^{-2}), carbon monoxide (1.0 kN m^{-2}), and a mixture of both gases, in cylinder air over platinum wire, are shown in Fig. 1. The results for hydrogen oxidation show a distinct kinetic region (320-360 K) with an

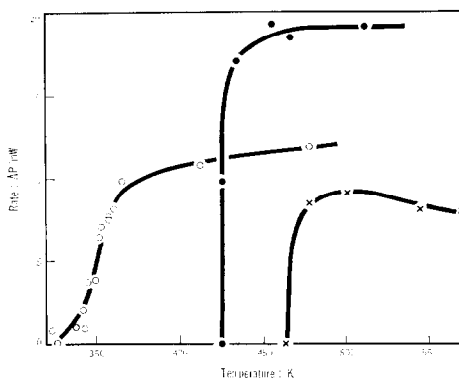


FIG. 1. Rates of oxidation over platinum wire. —○—, H_2 ($P = 0.5 \text{ kN m}^{-2}$); —×—, CO ($P = 1.0 \text{ kN m}^{-2}$); —●— CO ($P = 1.0 \text{ kN m}^{-2}$); and H_2 ($P = 0.5 \text{ kN m}^{-2}$).

apparent activation energy, $E_a = 80 \text{ kJ mol}^{-1}$, in good agreement with previous work (1). Above 360 K, the rate of reaction becomes limited by diffusion processes. In contrast, the results for carbon monoxide oxidation show a step from zero activity at 463 K to a diffusion-controlled regime at 478 K with a high apparent energy of activation, $E_a > 160 \text{ kJ mol}^{-1}$. The results for the gas mixture given in Fig. 1 indicate that it behaves as a single gas, with an apparent activation energy $E_a > 260 \text{ kJ mol}^{-1}$.

Oxidation of the mixture is first observed at 429 K. This temperature is 34° below that for carbon monoxide oxidation alone and 100° above that for hydrogen oxidation. Thus, in agreement with the work of Cohn (11) on supported platinum, the oxidation of hydrogen was found to be inhibited by the presence of carbon monoxide. However, at the same time there is a significant promotion of the carbon monoxide oxidation by hydrogen, not previously reported. All the other gas mixtures studied behaved similarly, with the relative positions of the curves dependent on the composition of the mixture. For clarity, therefore, the results have been summarized in Table 1 as the temperature at which oxidation is first observed (T_{\min}) and the maxi-

mum diffusion-controlled rate (ΔP_{\max}) obtained for each mixture. From the table it can be seen that, with the exception of mixture (7) [0.25 kN m^{-2} of H_2 , 0.5 kN m^{-2} of CO], the maximum rate of oxidation obtained for each mixture is the sum of the diffusion-controlled rates of oxidation of the components. It can also be seen that the degree of inhibition of hydrogen oxidation, as revealed by T_{\min} , is dependent on the partial pressure of carbon monoxide, just as the promotion of carbon monoxide oxidation is dependent on hydrogen pressure. Isothermal oscillations, observed separately in this laboratory (13), did not affect the measurements reported here.

In the oxidation of hydrogen over platinum wire it was suggested that an Eley-Rideal mechanism, with gas-phase hydrogen reacting with adsorbed atomic oxygen, is dominant under the present experimental conditions. Similarly, for carbon monoxide oxidation, the reaction between gas phase carbon monoxide and adsorbed oxygen is believed to be dominant (6, 7). However, it has been shown by Nishiyama and Wise (10) that at room temperature gas-phase carbon monoxide will react with adsorbed oxygen species to form gaseous carbon dioxide. The resulting vacant surface sites are filled by carbon monoxide, which is unable to react further with any

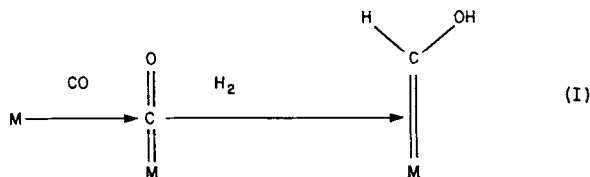
TABLE 1

Minimum Oxidation Temperature (T_{\min}) and Maximum Reaction Rate (ΔP_{\max}) for H_2/CO Mixtures

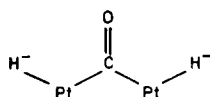
Expt. No.	P_{H_2} (kN m^{-2})	P_{CO} (kN m^{-2})	T_{\min} (K)	ΔP_{\max} (mW)
1	0.5	0	323	12
2	0.5	0.25	378	14
3	0.5	0.5	398	16
4	0.5	1.0	429	20
5	0	1.0	463	8
6	0	0.5	458	4
7	0.25	0.5	423	7
8	0.5	0.5	398	16
9	1.0	0.5	393	28

oxygen species. Similar observations were made at low pressure (typically 10^{-7} kN m^{-2}) by Bonzel and Ku (7), who further proposed that the rate-determining step of the oxidation reaction was desorption of carbon monoxide resulting in an apparent activation energy similar to the heat of adsorption of carbon monoxide. Our results are consistent with such a mechanism and our estimate of the apparent activation energy is in reasonable agreement with a calorimetrically determined (14) heat of adsorption of 200 kJ mol^{-1} . Thus we may predict a similar situation in the study of gas mixtures, wherein a platinum surface depleted in oxygen by the adsorption of carbon monoxide is presented to the reactant gas stream. Under such conditions hydrogen oxidation would be inhibited to the same extent as the oxidation of carbon

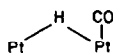
monoxide itself. That is, no reaction could be sustained until sufficient adsorbed carbon monoxide was removed from the surface to allow the dissociative adsorption of oxygen and the initiation of the rapid Eley-Rideal mechanism suggested by Bonzel and Ku. Nishiyama and Wise also suggested that the induction period they observed in the displacement of adsorbed hydrogen from a platinum surface by carbon monoxide was due to the formation of some binding state of hydrogen different from $H_{(ads)}$ in the absence of carbon monoxide. A complex $[H-CO]$ was suggested. Essentially similar species have been suggested as intermediates in the decomposition of formaldehyde (8) and in the methanation reaction (15) over other platinum group metals.



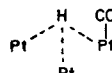
Infrared studies (9) have led several authors to suggest the formation of other adsorbed species:



(II)



(III)



(IV)

All four species may be expected to be less strongly bound, and hence desorb at a lower temperature than carbon monoxide alone. In species II to IV, $H_{(ads)}$ competes with $CO_{(ads)}$ for metal d-electrons, while species I does not have the capacity for $d - \pi^*_{CO}$ back-bonding of carbon monoxide. However, it is probable that the adsorbed hydrogen in species II to IV would be oxidized by gas-phase oxygen (3), resulting in a more complex temperature

dependency than the apparent single component response shown in Fig. 1. Thus it is proposed that a species of type I is formed, whose subsequent removal from the surface at a temperature below that necessary for carbon monoxide desorption is responsible for the observed kinetics of oxidation of gaseous mixtures of hydrogen and carbon monoxide over platinum catalysts.

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