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Oxidation Reactions on Platinum Catalysts

The kinetics of complete oxidation reactions over platinum catalysts have received relatively little attention in spite of their technical importance. It has proved relatively difficult to obtain reproducible results from kinetic studies on such catalysts (*1*) because oxidation or reduction of the catalyst surface can be caused by the reactants. Recent studies of methanol (*2*) and hydrogen (*3*) oxidation have shown that on well oxidized or reduced catalysts reproducibility can be obtained in atmospheres were oxygen or reducing gas, respectively, is in large excess.

Experiments using an excess of oxygen over a well oxidized platinum catalyst supported on a bead of α-alumina for the oxidation of methanol (*2*) showed that two parallel reactions occurred. The first type of reaction kinetics, hereafter referred to as type A, showed a zero order dependence on oxygen pressure and involved weakly adsorbed methanol molecules; the second type, hereafter referred to as type B, involved competitive adsorption between weakly adsorbed methanol molecules and oxygen atoms. However, studies of hydrogen oxidation on a well oxidized platinum wire showed that only the type A kinetics occurred. The experiments described here are an attempt to determine the cause of this difference in kinetic behavior and to see if any general kinetic mechanisms exist for oxidation reactions on platinum.

The difference in kinetics described above could be caused either by chemical differences between methanol and hydrogen or by the use of alumina as a carrier for the platinum used in the methanol study. Therefore we have studied the kinetics of the oxidation of carbon monoxide and methanol on different types of platinum catalysts. These results, together with those reported previously (*2*, *3*), enable a comparison to be made of the kinetics of oxidation of molecules containing in turn hydrogen atoms only, carbon and oxygen atoms only, and carbon, oxygen and hydrogen atoms on both platinum and platinum-on-alumina catalysts.

The experiments were carried out using a microcalorimetric technique, gas handling and catalyst preparation methods described previously (*2*, *3*). All experiments were performed using ratios of oxygen to reducing gas pressures of at least 5:1. Typical reducing gas pressures were 1 kN m^{-2}. Nitrogen was added as a diluent gas to bring the total pressure to 101 kN m^{-2}. Before use each catalyst was oxidized in air at 900°C (*3*).

In each case the reaction was first order in reducing gas at an oxygen pressure of 20.2 kN m^{-2} over the pressure range used showing that carbon monoxide (0–10 kN m^{-2} and methanol (0.3–3.7 kN m^{-2}) are all weakly adsorbed on both types of catalyst. The orders of each reaction in oxygen pressure were determined and the results are summarized in Table 1. It was not possible to study hydrogen oxidation on platinum on beads of alumina because the high reaction rates at temperatures above 0°C produced diffusion controlled reaction rates and at temperatures below 0°C ice was formed on the catalyst.

The results in Table 1 show that, with the above exception, type A reaction kinetics occur for all three gases on both types of catalysts. However, on platinum wires, type B kinetics occur only in carbon monoxide oxidation and not in the other two reactions. It is significant that water is a product in these two reactions. The ability of water to poison the sites for the type B reaction on this catalyst was confirmed by comparing the rates of oxi-

TABLE 1
PARTIAL ORDERS WITH RESPECT TO OXYGEN

Gas mixture	Partial pressure of reducing gas (kN m^{-2})	Platinum wire catalyst			Platinum on alumina catalyst		
		Order	Oxygen pressure range (kN m^{-2})	Temp range (°C)	Order	Oxygen pressure range (kN m^{-2})	Temp range (°C)
Hydrogen/oxygen	0.5	0	10–30	45–100	—	—	—
Carbon monoxide/oxygen	0.5	0 and $-\frac{1}{2}$	10–46	208–254	0 and $-\frac{1}{2}$	10–46	120–200
Methanol/oxygen	1.2	0	4–93	102–190	0 and $-\frac{1}{2}$	4–22	25–100

dation of carbon monoxide on platinum wires in the presence and absence of water vapor. The results are shown in Fig. 1. In this figure, ΔP is a measure of the heat evolved by the reaction and is directly proportional to the reaction rate (*3*). The presence of 3.1 kN m^{-2} of water vapor in the reactant gases completely eliminates the type B reaction, but the rate of the type A reaction is not affected. It has been proposed that the type A reaction in hydrogen oxidation has an Eley–Rideal mechanism involving oxide ions of a surface oxide species. It is probable that this is also the mechanism for this reaction for carbon monoxide and methanol and it is unlikely that such a reaction would be poisoned by water vapor or hydroxyl groups.

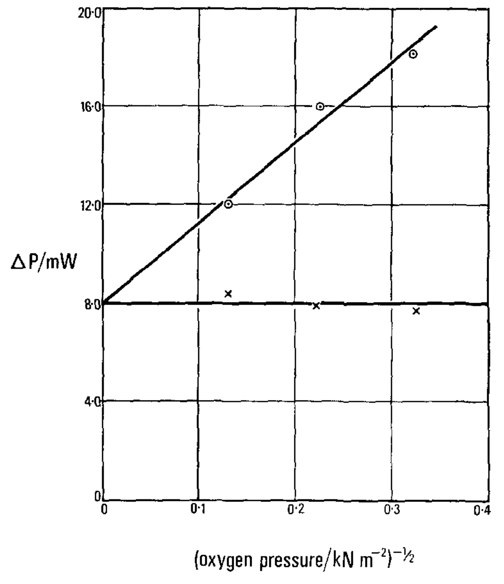

FIG. 1. Effect of water vapor on carbon monoxide oxidation: (⊙) Carbon monoxide; (×) carbon monoxide plus water vapor.

It is significant that both type A and B reactions occur in methanol oxidation on platinum on an alumina carrier. These kinetics were observed when either α- or γ-alumina was used as carrier material. This could be due to either (a) the alumina acting as a sink for adsorbed water or hydroxyl groups which poison the sites catalyzing the type B reaction, or (b) the difference in the crystal sizes of the platinum in the wire or on the alumina carrier. However, when the alumina carrier was replaced by one of fused glass and the catalyst was prepared in exactly the same way only the type A reaction took place in the temperature range 60–230°C. This indicates that alumina is capable of removing some of the adsorbed water or hydroxyl groups from the surface of the platinum which makes available some of the sites that catalyze the type B reaction.

Therefore, although water is adsorbed sufficiently strongly to poison the reaction on the sites that catalyze the type B reaction on platinum, it is still mobile enough on the surface to diffuse across to the alumina before desorbing. This would indicate that the heat of adsorption of water on oxidized platinum is low and hence that the heats of adsorption of oxygen, hydrogen, methanol and carbon monoxide on the type B sites are also low. The heat of adsorption of water on α-alumina is in the range 44–108 kJ mol^{-1}, depending on coverage (*4*), and hence the heats of adsorption of oxygen and the other reactants must be less than 108 kJ mol^{-1}. Boreskov (*5*) has reported heats of adsorption of weakly adsorbed oxygen on platinum of 54–100 kJ mol^{-1} and therefore it is this weakly adsorbed oxygen which is taking part in the type B reaction. Indeed, since water is a reaction product, it is likely that the alumina surface is fully hydroxylated and that the heat of adsorption of water will be near the lower end of the above range and hence that the heat of adsorption of oxygen taking part in the type B reaction is also very low.

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