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Oxygen Inhibition of CO Oxidation on Polycrystalline Rh

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The oxidation of CO on polycrystalline Rh has been investigated at low pressures and relatively high oxygen coverages using *in situ* mass spectrometry. Both transient and steady-state results clearly indicate that oxygen inhibits CO oxidation at temperatures greater than 550 K. The transient data also demonstrate that the reactivity of adsorbed oxygen depends upon the temperature at which it is formed and upon its surface organization. The observations are attributable in part to the formation of a surface oxide species which inhibits carbon monoxide adsorption.

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I. INTRODUCTION

The catalyzed oxidation of carbon monoxide over transition metals has been widely studied and yet interesting questions remain. Recent investigations have shown on Pd(111) (*1–3*), Ir(110) (*4*), polycrystalline Pt (*5, 6*), and polycrystalline Rh (*7, 8*) that this reaction occurs through the interaction of chemisorbed oxygen, O(a), and chemisorbed carbon monoxide, CO(a)—the Langmuir–Hinshelwood path. While this finding partially establishes the mechanism, the situation is still complex in that different temperature and coverage regimes are characterized by different rate laws (*2, 9*). We recently found that transient CO_2 production rates over polycrystalline Rh could be modelled for $T \geq 530$ K by assuming that O(a) inhibited the adsorption of CO(g) (*9*).

This model predicts an oxygen inhibition effect in steady-state experiments when the temperature and oxygen coverage are relatively high. For Pt (*10*) and Pd (*11*), which in many respects are like Rh, inhibition has not been observed in steady-state experiments. It was thus of considerable interest to search for and find, as reported here, a steady-state oxygen inhibition effect on Rh. While the structure which gives rise to inhibition has not been elucidated, we do find from transient experiments that O(a) reactivity depends upon the temperature at which it is formed and its maximum (initial) concentration.

II. EXPERIMENTAL

The experiments were carried out in an ion-pumped ultrahigh vacuum system with a routine base pressure of 5×10^{-7} Pa. As described previously (*9*), this system was outfitted with an ionization gauge, a mass spectrometer (calibrated with respect to the ion gauge), two gas inlet leak valves, a resistively heated polycrystalline Rh wire substrate (0.051 cm diameter × 14 cm long), and a chromel–alumel thermocouple. Sample cleaning and Auger verification of cleanliness have been discussed previously (*8*).

III. RESULTS AND DISCUSSION

Steady-State Kinetics

Steady-state rate measurements were made using three different oxygen pressures (2.0×10^{-6}, 1.0×10^{-5}, and 5×10^{-5} Pa) and a fixed carbon monoxide pressure (1×10^{-5} Pa). Since the system was continuously pumped, the measured partial pressure of carbon dioxide was proportional to its formation rate. Figure 1 is an Arrhenius graph of the results showing typical volcano-shaped plots (*8, 10, 12*) for each of the pressure ratios. As discussed elsewhere (*8*) the general shape of each of the curves can be understood in terms of: (1) low-temperature behavior where the CO(a) desorption rate plays a major role, (2) intermediate temperature where the

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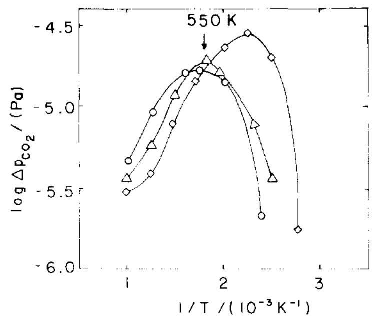

FIG. 1. Dependence of the CO_2 production on temperature at three different oxygen pressures. The oxygen presures are 2×10^{-6} Pa (○), 1×10^{-5} Pa (△), and 5×10^{-5} Pa (◇). The CO pressure is 1×10^{-5} Pa in all cases.

coverages of CO and O are relatively small (adsorption probabilities are large but reaction probabilities are just as large or larger), and (3) high temperatures where sticking probabilities and residence times for both CO and O_2 become smaller.

For our purposes here, the interesting feature of Fig. 1 is the inversion of the order of the three curves which occurs near 550 K. Below this temperature the rate increases as the oxygen pressure is increased whereas above it the reverse holds. The transition temperature, 550 K, is in excellent agreement with our previous analysis (*9*) of transient results which suggested that oxygen inhibition of CO adsorption set in at about 530 K. On Pt (*10*) and Pd (*11*) there is no inhibition observed in equivalent steady-state experiments. Inhibition has been noted, however, on Ag(110) (*13*) and on Rh(100) at low temperatures (*14*).

Transient Experiments

In an effort to determine some of the factors which give rise to oxygen inhibition, we have examined two kinds of transient experiments. In the first, a fixed initial oxygen coverage[1] ($\theta_0{}^i = 0.83$) was established at two different temperatures (T = 350 and 780 K) and was titrated at 320 K using a fixed CO leak rate (final CO pressure = 6×10^{-6} Pa). The results, shown in Fig. 2, show that O(a) formed at high temperatures is less reactive than that formed at low temperatures. Thus inhibition is at least partially related to temperature-dependent variations of the form which oxygen takes on the surface. According to our model (*9*), the high-temperature form of oxygen reacts to produce CO_2 with a much higher activation energy than the low-temperature form and the high-temperature form inhibits CO adsorption. For Rh(111) there is recent LEED and AES evidence (*15, 16*) that a structural change in chemisorbed oxygen does indeed occur at relatively low temperatures (≃ 400 K) and is associated with penetration of oxygen into the outer layers of the Rh lattice. The formation of this structure which we believe is more like an oxide than chemisorbed oxygen may be responsible for the reactivity changes noted in Fig. 2. It is important to note that the sample of Fig. 2b was cooled in oxygen to avoid background titration effects. Thus not all the oxygen was adsorbed at 780 K. This does not, however, jeopardize the qualita-

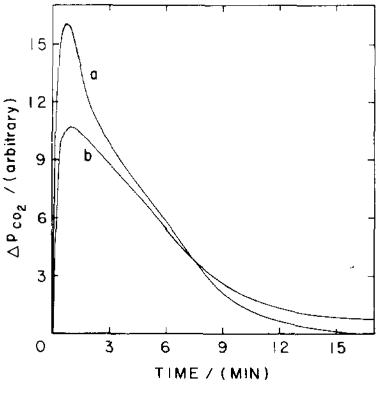

FIG. 2. CO_2 production at 320 K as a function of time for different preparations of $\theta_0{}^i$ = 0.83. (a) Oxygen was adsorbed at 2.8×10^{-5} Pa for 4 min in the range 350–320 K. (b) Oxygen was adsorbed (2.8×10^{-5} Pa) for 2 min at 780 K and for another 2 min while the sample was cooled down to the final temperature 320 K. Integral to curve b to longer times gives the same area as curve a.

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[1] Oxygen coverages are measured with respect to saturation values achieved at 320 K and are determined by measuring areas beneath CO_2 titration or O_2 flash desorption curves.

tive conclusion that the high-temperature form of oxygen is less reactive.

The interpretation is even more complex, however, because transient rates at constant oxygen coverage and temperature vary depending upon the initial oxygen coverage. An example is given in Fig. 3 where transient CO_2 production rates are plotted as a function of $(1 - \theta_0)$ or θ_0 for T = 630 K and two initial oxygen coverages ($\theta_0{}^i$ = 1.0 and 0.81). In both cases the CO input rate gave a final (after all O(a) was titrated) pressure of 5.7×10^{-6} Pa and the transients required more than 8 min to complete. At 630 K, the steady-state carbon monoxide coverage is very small ($\theta_{CO} < 10^{-4}$) when θ_0 = 0 and is even smaller in the presence of O(a). According to the data of Fig. 3, the transient CO_2 production rate for $\theta_0{}^i = 0.81$ exceeds that for $\theta_0{}^i = 1.0$ over the range $0.25 < 1 - \theta_0 < 0.9$. For any value of $(1 - \theta_0)$ in this range, the total CO exposure is larger for $\theta_0{}^i = 1.0$ and, if the oxygen structures in the two cases were equivalent, the carbon monoxide coverage, and the carbon dioxide production rate, would be the same or lower for the $\theta_0{}^i = 0.81$ case. Since this is not observed, we conclude that the oxygen structures present are inequivalent over the range $0.25 < \theta_0 < 0.90$ and, by inference, are structurally different initially. Yates *et al.* (*16*) have noted, at lower temperatures and on Rh(111), that massive ordering occurs in the last stages of oxygen adsorption and that the kinetics of subsequent reaction with hydrogen differ with the nature of the ordering. Similar coverage-dependent structural forms and reaction kinetics can be invoked as a model to describe the observations shown in Fig. 3, but no direct assessment can be made on a polycrystalline wire substrate using LEED (*15*). Although such investigations on single crystal faces may be difficult, particularly at elevated temperatures, it is clear that measurements distinguishing various organizations of oxygen at equal coverages would be particularly helpful.

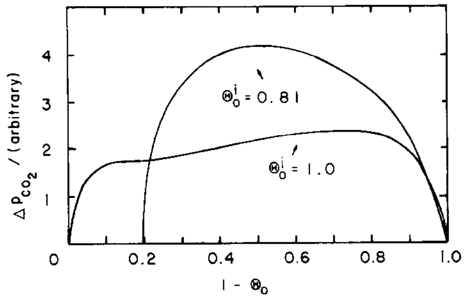

FIG. 3. CO_2 production at 630 K as a function of $(1 - \theta_0)$ for two initial coverages of 1.0 (a) and 0.81 (b).

In passing it should be noted that flashing the Rh, with both forms of oxygen present, furnishes a clean surface. This implies that oxygen either desorbs or dilutes in the bulk. Furthermore, flash desorption following CO titration gives no measurable O_2 desorption and indicates that all near-surface oxygen is removed by reaction to form CO_2.

IV. SUMMARY

The results reported here can be summarized as follows:

(1) A steady-state inhibition of carbon dioxide production by chemisorbed oxygen has been observed for $T > 550$ K on a polycrystalline rhodium wire catalyst. The transition temperature (550 K) agrees well with the onset of inhibition of carbon monoxide adsorption predicted in earlier work.

(2) Transient titration experiments at 320 K show that the reactivity of O(a) formed at 780 K is significantly lower than that formed at 340 K. This is ascribed, at least partly, to penetration of oxygen into the near-surface region at high temperatures.

(3) In transient experiments at 630 K, the reactivity to form CO_2 at constant θ_0 varies with the initial coverage of oxygen. This is interpreted in terms of oxygen structural differences perhaps the extent of ordering, which are present initially and throughout most of the transient.

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