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Carbon Monoxide Oxidation Over Ru (001)

Whereas Pt (1), Pd (2), Rh (3), and Ir (4) foils, wires, and single crystals are all excellent catalysts for the CO oxidation reaction at low pressures, Ru is not and, as reported here, the maximum reaction probability per CO collision under comparable pressure conditions is about 5% of that observed for Rh (5). Differences in the characteristics of this reaction over (001), (101), and supported Ru have been reported which do not exist for other transition metals. For example, on Ru (001) it has been reported (6) that the maximum steady-state CO_2 production for $p_{CO} = p_{O_2} = 4 \times 10^{-7}$ Torr occurs at about 950 K while on Ru (101) the maximum was found near 730 K (7). On silica-supported Ru, exposed at 760 Torr to air containing 100–200 ppm CO, the rate maximized near 530 K (8). In contrast, Pd shows no differences of significance between single-crystal faces, supported catalysts, wires, and foils (2). In this paper we report steady-state CO_2 production rates over the basal plane (001) of Ru which maximize in the region between 450 and 500 K and thus follow much more closely the supported catalyst results than earlier data on this crystal face (6).

The experiments were carried out in a small (about 1.5 liter) conductance-limited ultrahigh vacuum chamber operating at a typical CO-dominated background pressure of 1.5×10^{-9} Torr. The substrate was connected to massive tungsten heater leads using small Ru connective rods cut from a single-crystal boule. These were designed to give uniform heating of the sample and leads. A W–W, 26% Re thermocouple was spot-welded to the rear of the crystal. Systematic cleaning procedures involving high-temperature oxygen treatment were established using Auger electron spectroscopy (AES) in a separate chamber. These followed closely procedures outlined in the literature (6, 9). In the small chamber where kinetic measurements were made the diagnostic for a clean surface after a standard oxygen treatment was a characteristic two-peaked CO-saturated desorption spectrum (10). As outlined elsewhere (11) this spectrum is very sensitive to small amounts of impurities, particularly the residual oxygen sometimes present after cleaning.

In Fig. 1 the steady-state rate of CO_2 production, measured as the increase over the room-temperature rate, is plotted as a function of temperature. The pressure of CO and O_2 were each fixed at 1×10^{-7} Torr using leak valves and the system was pumped constantly. According to Fig. 1 the maximum CO_2 production rate occurs at about 475 ± 25 K and, just as with other transition metals, the rate grows as CO desorbs (1–4). This rate profile was obtained for experiments in which the temperature was both increased and decreased and is qualitatively similar to those found for silica-supported Ru (8, 12). At the maximum of Fig. 1, the reaction probability per CO collision is 0.04.

In a separate experiment, the rate of CO_2 production was measured as a function of CO pressure for fixed $T = 475$ K and $p_{O_2} = 1 \times 10^{-7}$ Torr. Figure 2 shows the results which are reminiscent of those found on other transition metals except the rates are much smaller. At low relative CO pressures, the production of CO_2 is first order in CO pressure whereas at high CO pressures the rate becomes zero order in CO.

Figure 3 shows the results of AES titration experiments done at 500 and 900 K.

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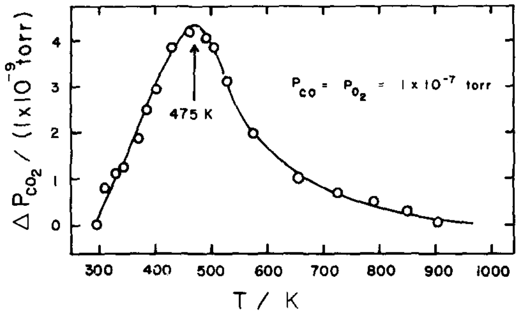

FIG. 1. Steady-state CO_2 formation rate as a function of temperature. p_{CO_2} is the increase over the room-temperature rate, and the pressure of CO and O_2 were each fixed at 1 × 10^{-7} Torr.

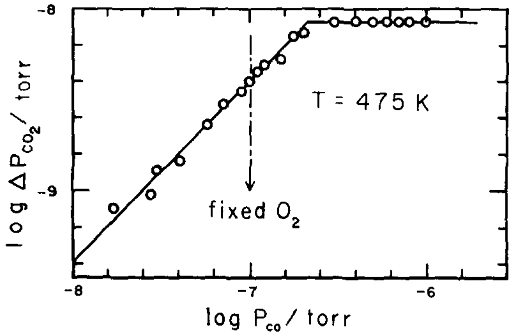

FIG. 2. Steady-state CO_2 formation rate as a function of CO pressure for fixed T = 475 K and p_{O_2} = 1 × 10^{-7} Torr.

These involve heating an oxygen-saturated Ru surface in the presence and absence of CO. Electron-beam-induced dissociation of CO is negligible because at both temperatures CO coverages are small and because the time under the electron beam is minimized. Saturated surfaces were prepared by an exposure of 100 liters of O_2 at either 500 or 900 K. After a brief evacuation the sample was exposed to 8 × 10^{-7} Torr of CO and the AES signal for oxygen, relative to one of the strong transitions for Ru, was followed. For comparison the same experiment was repeated omitting the exposure to carbon monoxide. With the CO leak valve closed, the level of the oxygen signal declined slowly at 900 K but remained nearly constant at 500 K. With CO present, the oxygen signal declines at both temperatures but clearly more rapidly by at least a factor of four at the lower temperature. In a separate experiment, the initial conditions of Fig. 3 were established again but the electron beam was on (for AES) only at the start and after a 2400-liter CO exposure at 2 × 10^{-6} Torr. The decay rates were the same as those shown in Fig. 3. Comparing reaction probabilities per CO collision, the data of Fig. 1 furnish values of 4 × 10^{-2} at 500 K and 5 × 10^{-3} at 900 K whereas Fig. 3 gives 2 × 10^{-3} at 500 K and 4 × 10^{-4} at 900 K. There is considerable uncertainty in these values but qualitatively, the steady-state rate (Fig. 1) is about one order of magnitude larger than the transient rate (Fig. 3). As discussed below, we believe the difference may arise because a small fraction of the oxygen-containing sites is much more active for CO_2 production than the remainder and that, in the presence of CO, these highly active sites are significantly populated only when gas-phase oxygen is present. Another set of experiments lends support to the idea that adsorbed oxygen exists in configurations of differing reactivity. When a coadsorbed mixture of O_2 (1 liter) and CO (1 liter), dosed in this order at 300 K, is flashed, the transient amount of CO_2 produced is about 4 times larger than when the adsorbed oxygen is momentarily heated to 650 K before exposure to CO. This suggests that annealing surface oxygen

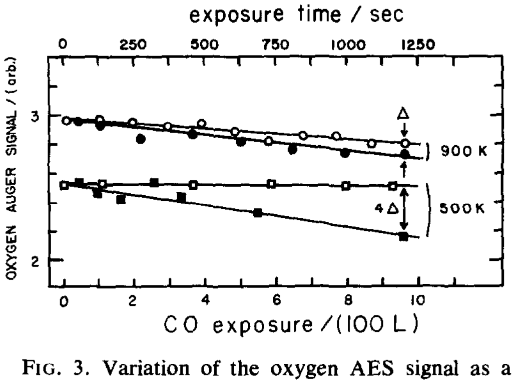

FIG. 3. Variation of the oxygen AES signal as a function of CO exposure (by the pressure of 8 × 10^{-7} Torr) on oxygen-saturated surfaces at 500 K (■) and 900 K (●). As references, the time dependences of the oxygen AES signal in the absence of CO exposure are shown for 500 K (□) and 900 K (○).

changes its structure and lowers its reactivity towards impinging CO.

Our steady-state results are somewhat different from those reported by Madey *et al.* (*6*). We find a maximum near 475 K whereas they find it to be near 950 K. In other respects the results are identical within experimental error. For example there is genuine agreement as to LEED patterns for adsorbed carbon monoxide and oxygen, flash desorption spectra for CO and O_2, sticking coefficients for CO and O_2, and the generally low probability for forming CO_2. Thus the diverging results for the temperature dependence of CO_2 production are exceptional.

While we cannot attribute this difference to any particular source there are several points to consider, some relating to experimental design and others to the detailed character of the surface. We simply enumerate these as follows:

(1) Madey *et al.* (*6*) used a thermocouple comprised of Pt and Rh which are both very active CO-oxidation catalysts. We used W and Re which are at least as poor as Ru. Low-area thermocouple wires of relatively high activity could cause the apparent production peak at high temperature as the result of a temperature gradient along their lengths.

(2) Oxygen penetration is significant when an oxygen-covered surface is heated and must be accounted for in any AES or LEED experiment involving temperatures greater than about 500 K (*9*).

(3) Since the CO reaction probability is very small, the surface will be oxygen rich (almost saturated at all the conditions shown in Fig. 2). This observation suggests that CO_2 production involves a particular kind of oxygen, determined by the site, which is present in very low concentration.

(3) Since the CO reaction probability is very small, the surface will be oxygen rich (almost saturated at all the conditions shown in Fig. 2). This observation suggests that CO_2 production involves a particular kind of oxygen, determined by the site, which is present in very low concentration. Given the rather complex behavior of oxygen on Ru (*9, 13*) and the unknown differences in the numbers of defects on the Ru crystals employed, it is thus possible that (001) surfaces giving the same LEED and flash desorption spectra could give very different CO_2 production rate profiles.

We have no means of ascertaining the extent to which these may have contributed to the divergent results. However, we have found no experimental condition for which the maximum rate occurs at a temperature significantly higher than 475 K. The third point deserves additional attention. Several factors could have some influence on the concentration of active oxygen: (1) the details of the Ru surface, (2) the concentration and structure of subsurface oxygen, and (3) the concentration and structure of surface oxygen.

Fuggle *et al.* (*14*) report that about 15–20% of the oxygen XPS intensity is lost when a surface saturated in oxygen at 300 K is exposed to carbon monoxide also at 300 K. Further exposure at 300 K does not alter the XPS signal arising from chemisorbed oxygen. These observations suggest that under oxygen-presaturated conditions a small fraction of the total oxygen may be reactive. Under steady-state conditions at 300 K the rate would be very small due to CO inhibition while around 475 K where CO desorbs, but still has a long surface residence time, the adsorption of oxygen would occur readily on a small number of sites and chemisorption rates of CO and O_2 could be balanced by adjusting their relative pressures. Thus working at 475 K as in Fig. 2, the CO_2 production rate would be determined by the CO collision frequency for $p_{CO}/p_{O_2} < 2$ while the O_2 adsorption rate would be determining at higher ratios. Thus, the XPS data (*14*) and all the data reported here are consistent.

Regarding oxygen coverages, the LEED data of Madey *et al.* (*6*) involved beginning with a surface half-saturated in oxygen which may have a different reactivity than a saturated surface. There is, as noted above, a quantitative difference between the steady state and transient rates measured under nearly saturated conditions. If only a small fraction of the surface oxygen is highly reactive and if this fraction involves sites populated only at very high coverage, then the higher apparent reaction probability under steady-state conditions can be easily understood. The presence of gas-phase oxygen drives the oxygen coverage to slightly higher values than when the oxygen pressure is removed and these sites are responsible for the high activity under steady-state conditions.

Under the conditions of the silica-supported Ru work (*8*) where $p_{CO}/p_{O_2} \simeq 10^{-4}$ we expect the surface to be very oxygen rich but capable of adsorbing CO (*11*). At low temperatures then, we can envision CO competing with oxygen for adsorption sites in much the same way as described above for the low-pressure experiments.

It is important to note that the results of Reed *et al.* (*7*) on Ru (101) are clearly distinct from the data on Ru (001). For one thing the oxygen adsorption rate on (101) is markedly lower but the adsorbed oxygen is apparently much more reactive toward CO. However, these results are also subject to some uncertainty due to the use of a Pt–Rh thermocouple. Second, an oxygen-saturated (101) surface does not chemisorb CO at 300 K whereas on (001) an oxygen-saturated surface readily adsorbs CO with a sticking coefficient comparable to that of a clean surface (*11*).

In conclusion, we find CO_2 production profiles on Ru (001) which have features found on Pt, Pd, Rh, and Ir, except the rates per unit surface area are about an order of magnitude lower. The results are consistent with a model for which only a small fraction of the surface oxygen is reactive towards CO. We also find that annealing adsorbed oxygen prior to exposure to carbon monoxide lowers its reactivity significantly.

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