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Exo-Electron Emission During Heterogeneous Catalysis (the Effect of External Electric Potentials)

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Exo-electron emission was observed during catalytic oxidation of CO, H_2 or NH_3 on hot platinum. The exo-electron current level was related to the rate of reaction. Suppressing or enhancing the exo-electron current decreased or increased the rate of reaction.

I. INTRODUCTION

The emission of electrons by solids during adsorption or reaction has been reported many times. Typical examples are: Hartley (*1*), Finch (*2*), Denisoff and Richardson (*3*) and Delchar (*4*). In all of these cases the mechanism was not clear but it was suggested that the reaction disturbed the metal surface and somehow permitted electrons or ions to "leak out."

This type of phenomena is now well known and is usually called exo-electron emission (EEE). In view of the close connection between adsorption and heterogeneous catalysis one might expect that heterogeneous catalysis would be accompanied by copious exo-electron emission. This effect was reported by Sato and Seo (*5*) who observed a linear relation between the rate of reaction and exo-electron emission. Similar studies were reported by Momose and Tamai (*6*). These results ranging from oxidation of ethylene on AgO (*5*) to the reduction of CuO by ethanol (*6*) suggest that exo-electron emission occurs as part of many heterogeneous catalytic reactions. In our study we sought for similar phenomena during oxidation of NH_3, H_2 or CO over platinum.

If exo-electron emission is part of a catalytic reaction one might ask if it is a necessary step in the process or if it simply occurs but has no effect on the reaction evidence that EEE has an effect upon the rate of catalysis in the sense that enhancement or suppression of EEE increases or decreases the rate of reaction. Typical studies in this area are those of Stadnik and Fensik (*7*) who observed that a negative bias on silver catalyst increased the rate of oxidation of various alcohols. The effects were observed with low (10–15 V) voltages which would be large enough to influence low energy exo-electrons. Other work by Stadnik and Sekeresh (*8*) on the oxidation of methane over zinc oxide indicated that biasing the catalyst with a negative voltage increased the rate of reaction. The voltage levels in this case were substantially higher (200 V) than those used in (*7*).

A recent paper by Vladov and his associates (*9*) reports the effect of a negative bias on the catalyst as increasing the rate of decomposition of ammonia on a Pt–Rh–Pd alloy. In (*9*) the authors admit of the possibility that exo-electron emission may be the driving effect, but feel that the evidence is insufficient for drawing final conclusions.

Other work by Lee (*10*) and Kester (*11*) showed that ac electric fields at specific frequencies had effects on catalytic reactions. However, their use of ac makes it diffiult to interpret their work.

Our results suggest that the application of dc bias voltages to the catalyst *before* itself. Here there is some circumstantial the catalyst is heated, to start the reaction, can enhance or suppress the exo-electron emission thereby increasing or decreasing the rate of catalysis. These phenomena offer the opportunity for improved techniques for the monitoring and control of heterogeneous catalysis.

II. Experimental Studies

A. Apparatus

The system is shown in Fig. 1. The mass spectrometer was an EAI Quad 250 which was used to control the gas mixture in the system and to monitor product peaks during catalytic reactions. The catalysts were in the form of 3 wires each 0.25 mm in diameter, twisted into a rope-like configuration. The catalyst material was commercial platinum (99.99%). The catalyst filament was heated by ac current with an isolated power supply. Filament temperatures were monitored by a welded-on thermocouple. The catalyst wires could be biased at any value from 0 (ground) to ±900 V by means of a Fluke power supply. The exo-electron currents were collected by a stainless steel collector biased at +24 V, and measured with a Keithley 417 picoammeter. The vacuum system was stainless steel, with copper gaskets, pumped to 10^{-5} Torr by an oil pump and to 10^{-9} Torr by a 50 liter/s Vac-Ion pump. The oil pump was isolated from the system during the catalysis experiments. Tests to determine if the Vac-Ion pump was producing any signals in the electron measurement system were negative.

Experimental studies were made of the catalytic oxidation of CO, NH_3 and H_2. The gases were commercial grade taken from standard cylinders. The gas input was controlled by Granville-Phillips leak valves. Partial pressures were monitored by a discharge gauge and the Vac-Ion pump current. All oxidation experiments were run at a total pressure of 6×10^{-6} Torr. The CO, H_2 or NH_3 partial pressures were held at about 1×10^{-6} Torr during the experiments.

B. Experiments and Results

Investigation of the background effects involved grounding the filament (catalyst) and biasing the collector at +24 V, with the vacuum system pumped to 10^{-8} Torr. Then each of the gases we planned to use was admitted until the system reached a pressure of about 10^{-6} Torr. For each gas, the platinum filament was slowly heated from 20 to 800°C while the mass spectrometer and the picoammeter were used to look for spurious signals. No reaction products were observed, but there was some exo-electron emission due to changes in the work function of the filament induced by chemisorption and surface rearrangement.

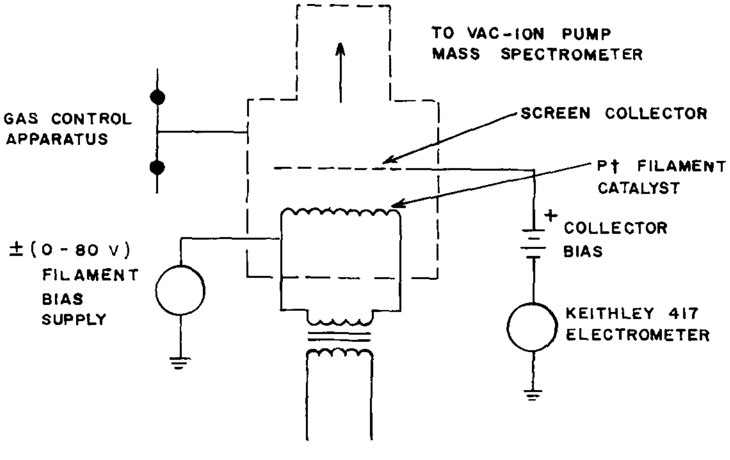

FIG. 1. Exo-electron catalysis experimental system.

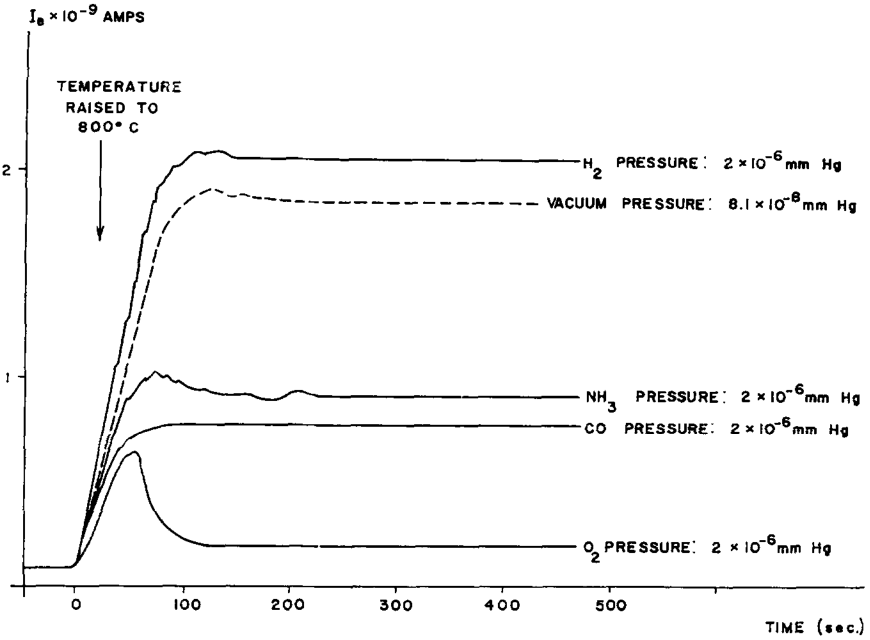

FIG. 2. Effect of various gases on exo-electron emission from platinum.

The effects are shown in Fig. 2. Oxygen increases the work function and hydrogen reduces it. CO and NH_3 reduce the emission below the vacuum level.

The first platinum catalysis studies were done with CO and O_2. Here the rate of catalysis was small at room temperature but rose rapidly as the catalyst was heated to the operating temperature, 775°C. The exo-electron emission followed the rate of catalysis as shown in Fig. 3. Here the height of the CO_2 peak (K) in arbitrary units and the exo-electron current (I_e) in amperes, are plotted as a function of time.

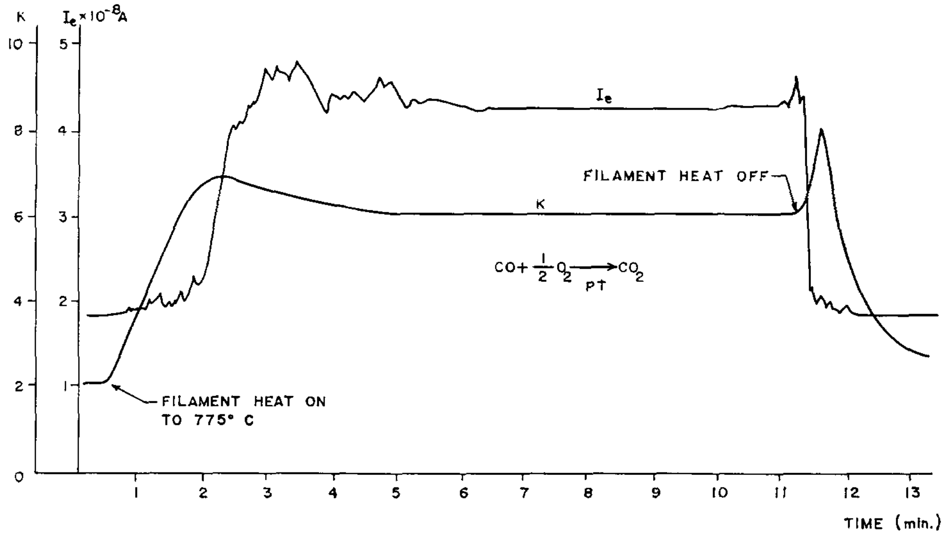

FIG. 3. Rate of reaction and exo-electron emission versus time—oxidation of CO.

Notice that the exo-electron current follows the rate of reaction and is somewhat erratic until (K) bcomes constant, at which time I_e drops to a slightly lower level. This phenomena was quite consistent and a series of experiments at higher and lower filament temperatures indicated that the time for the drop to occur decreased with increased filament temperature. For example, at 800°C, (K) reached equilibrium in 3 min and I_e fell to the lower level value. At 700°C a longer time (7 min) was required before (K) reached a constant value and I_e fell to the lower level. It seems that once equilibrium is established, the situation is quite stable. Raising or lowering the catalyst temperature by 50°C did not appreciably change (K) or I_e.

Notice in Fig. 3 the surge that occurs whenever the heating current to the filament is turned off. This surge is of considerable interest and was observed *whenever* the catalyst was allowed to cool quickly to 20°C from its operating temperature. We must emphasize that this is *not* a switching transient, the decay time is far too long. If the filament was allowed to cool slowly (by reducing the heating current over some 3 min), the surge was not observed, the (K) and I_e curves simply decreased to their 20°C values. Data presented below demonstrate that the "decay mode" is also dependent upon the filament bias and we suggest that surface mass migration is responsible for the "cooling" surge in exo-electron emission.

It is interesting to note that the effect of heat-up and cool-down rates on catalytic activity has been observed before. Bernstein *et al.* (*12*) commented that the reduction of NOx over monel requires that the catalyst be heated rapidly if it is to be effective. Our system did not permit careful control of heat-up or cool-down rates, and for this reason the heating current was usually turned on and off with a snap switch.

Our other experiments, on oxidation of H_2 and NH_3, yielded qualitatively similar results which need not be presented in graphical form. The features discussed above in the CO studies were easily observed. We must note that all our reported values of (K), the reaction rate constant, are only relative. The effects of CO, NH_3 and O_2 on the Quad-250 electron multiplier made it impossible to correlate our (K) values with those in the literature. However, once the multiplier had not been stabilized with a particular gas mixture there was no further drift over many hours of operation.

To demonstrate that exo-electron emission could be used to obtain activation energies we measured (K) and I_e over a range of temperatures for the carbon monoxide oxidation process. The data are shown in Fig. 4. The I_e curve follows the (K) curve until thermal emission begins to be significant, at which point I_e becomes very large. This almost linear relationship between (K) and I_e was also observed with NH_3 and H_2 but with different numerical values. (The positive ion current emitted by the filament, during the reaction, is also shown in Fig. 4. This is discussed in the Appendix.)

The data of Fig. 4 can be used to obtain an activation energy (E) by writing the Arrhenius equation in the form

$$\log_{10} K = \log_{10} A - \frac{E}{2.303RT}.$$

If we choose two values of (K) at two temperatures, the equation takes the form

$$\log_{10} \frac{K_2}{K_1} = \frac{E}{2.303R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

which can be solved for E.

Using the data of Fig. 4 we chose

$$T_1 = 500°\mathrm{C} = 773°K,\ K_1 = 5.3,$$
$$T_2 = 600°\mathrm{C} = 873°\mathrm{K},\ K_2 = 8.3,$$
$$R = 1.99\ \mathrm{cal}/°\mathrm{K\ mole},$$

and obtained $E = 6.7 \times 10^3$ cal/mole. This may be compared with the data of Heyne and Tompkins (*13*), where an activation energy of 10×10^3 cal/mole was obtained. This agreement may be somewhat fortuitous because a supported platinum catalyst at lower temperatures (300°K) was used in the work (*13*). Nevertheless, our agree-

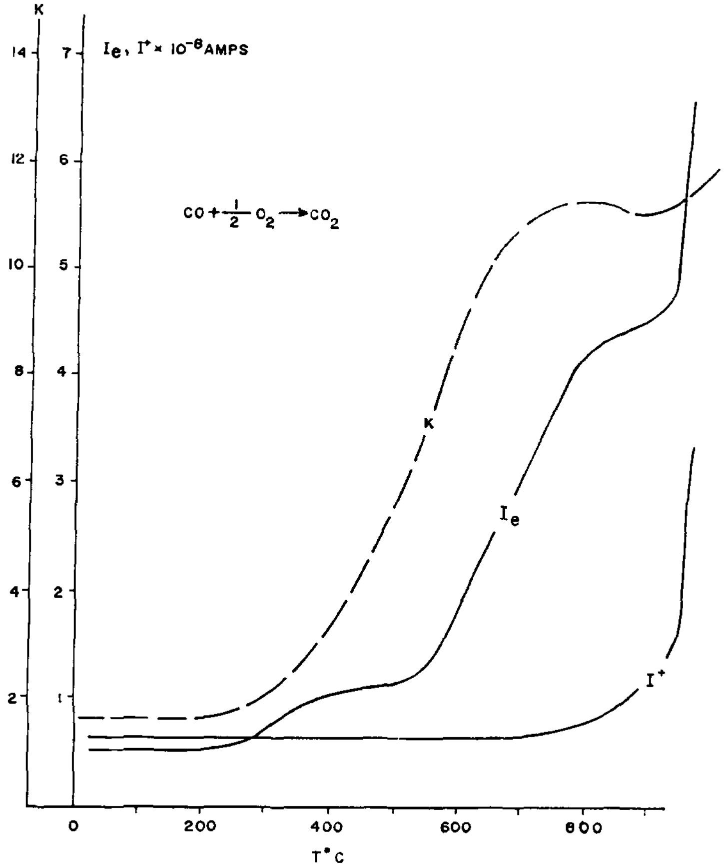

FIG. 4. Rate of reaction and exo-electron emission versus temperature—oxidation of CO.

ment with the generally accepted value of (E) is encouraging.

At this point we began to investigate the effects of external electric fields on catalysis and exo-electron emission. Here again we note that *whenever* a particular experimental effect is reported with CO, H_2 or NH_3, the same experiment was repeated with the other two gases. If the results were qualitatively similar no further discussion is given. If there were significant differences, this is discussed in the text.

In the first electric field experiments we wished to see what effect, if any, would occur if we biased the catalyst to reduce or enhance exo-electron emission. For these experiments the catalyst was raised to its operating temperature (770°C) and then biased with the Fluke power supply to ±28 V. The first experiments indicated that changing the catalyst bias *during* a catalysis run did change the value of I_e. However, the value of (K) was unaffected and this suggested that electric fields had no effect on catalysis.

This idea was found to be incorrect when we tried applying the bias voltage to the filament *before* heating it to begin catalysis. Typical results are shown in Fig. 5 for oxidation of CO, a −28 V bias increased *both* (K) and I_e over the "no-bias" values which are not shown to avoid confusion in the figure. Conversely, a +28 V bias decreased *both* (K) and I_e below the no-bias values. More detailed data on the effects of changing filament bias is shown in Fig. 6 for CO oxidation. Here the bias was changed each time the filament was cooled to 20°C. Then the catalyst was heated to 770°C again and held at that temperature until (K) was effectively constant. At this time the heating current was

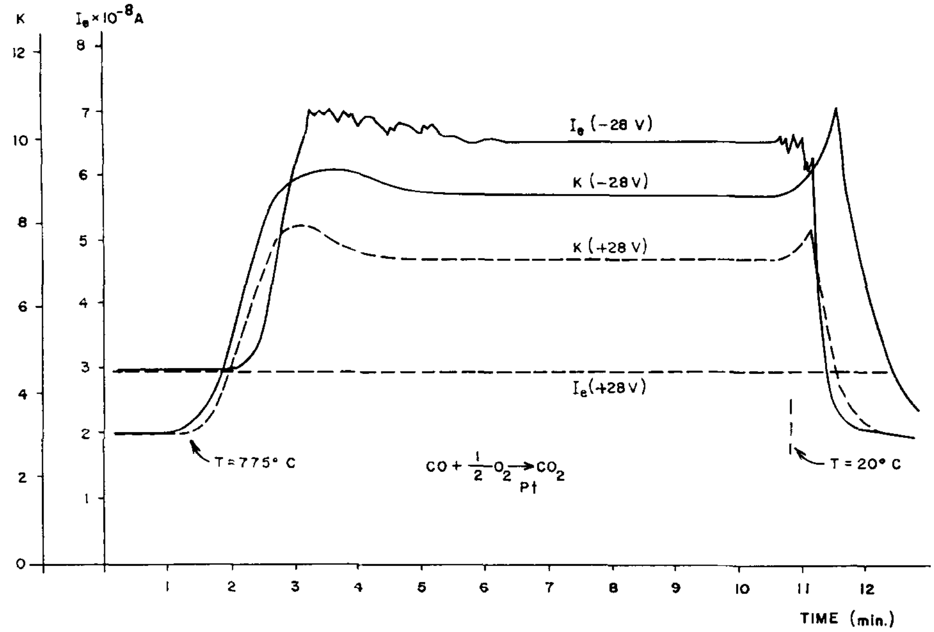

FIG. 5. Effect of an external electric field on catalysis of CO oxidation.

removed and the filament cooled to 20°C.

As we expected, the higher negative voltages yielded higher (*K*) values. More surprising is the way in which (*K*) rises (upon heating) and falls (upon cooling). At high voltages (−83 *V*) the rise is rapid and the drop is preceded by a steep pulse which dies away very rapidly. At −30 V the rise

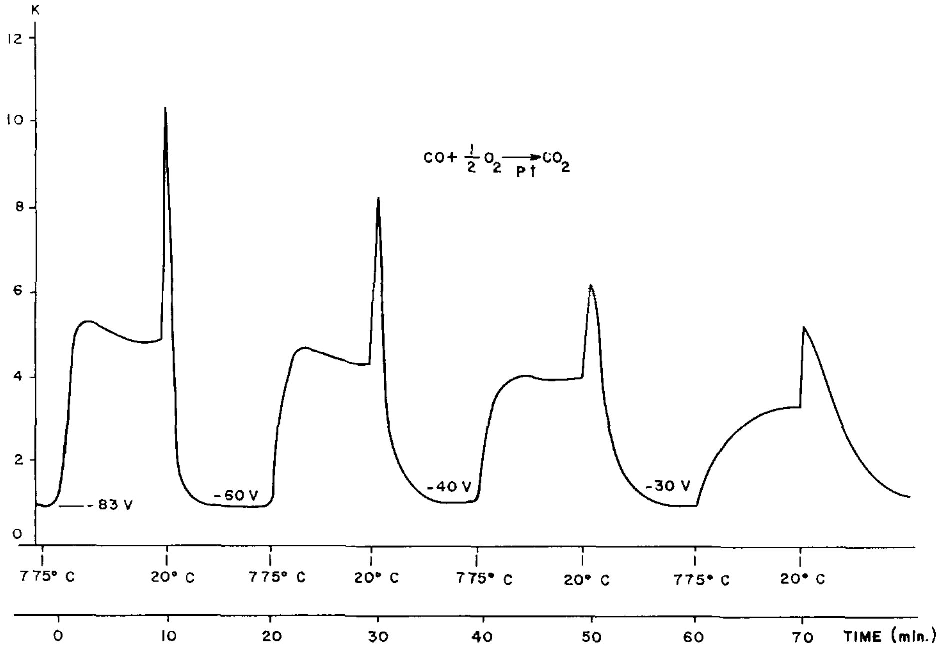

FIG. 6. Effect of various filament voltages (—) on catalytic oxidation of CO.

occurs much more slowly and the decay is significantly longer. There seems to be some sort of surface change which depends upon the filament voltage both in absolute value and in the rate of approach to equilibrium.

A similar experiment at a series of positive filament bias voltages indicated that +28 V reduces both I_e and (K). Increasing the filament bias in steps to +80 V reduced I_e to almost zero but had no effect on (K). Apparently the effect of a postive filament bias on the rate of catalysis (K) is complete at +28 V. In contrast, (K) increases with negative filament bias up to about −100 V.

There is direct evidence that a postive filament bias not only reduces (K) but it can condition the filament against catalysis. Evidence of this effect is shown in Fig. 7. Here we have plotted (K) versus time (oxidation of CO) for a filament that was first biased at +30 V to retard exo-electron emission. The filament was then cooled to 20°C and −30 V was applied. An increased value of (K) was observed but it was *significantly lower* than that usually observed at −30 V. We suspected that the +30 V exposure had somehow "formed" the catalyst into an ineffective state. The catalyst was heated to 950°C in vacuum without any applied potential, then cooled to 20°C. The −30 V was reapplied and the catalytic run was repeated. The value of (K) was that normally observed with −30 V potential suggesting that the +30 V potential had "formed" the catalyst and the heating at 950°C had "annealed" the material.

One study was done to determine if the emitted exo-electron current had a complex energy spectrum. If such a spectrum existed it might be related to the presence of "activated complexes" as reaction intermediates. For this experiment the catalytic oxidation reaction was allowed to stabilize with the filament held at ground potential, then the filament voltage was raised in steps to +33 V. The exo-electron current decreased each time the voltage increased. No structure in the I_e versus voltage curve was observed. This suggests that no reaction intermediates are involved in the exo-electron emission.

III. Discussion and Conclusion:

It seems quite clear that exo-electron emission may be used as a measure of the rate of certain catalytic reactions. The induction phase and the approach to steady state can be observed without ambiguity in terms of exo-electron emission. The

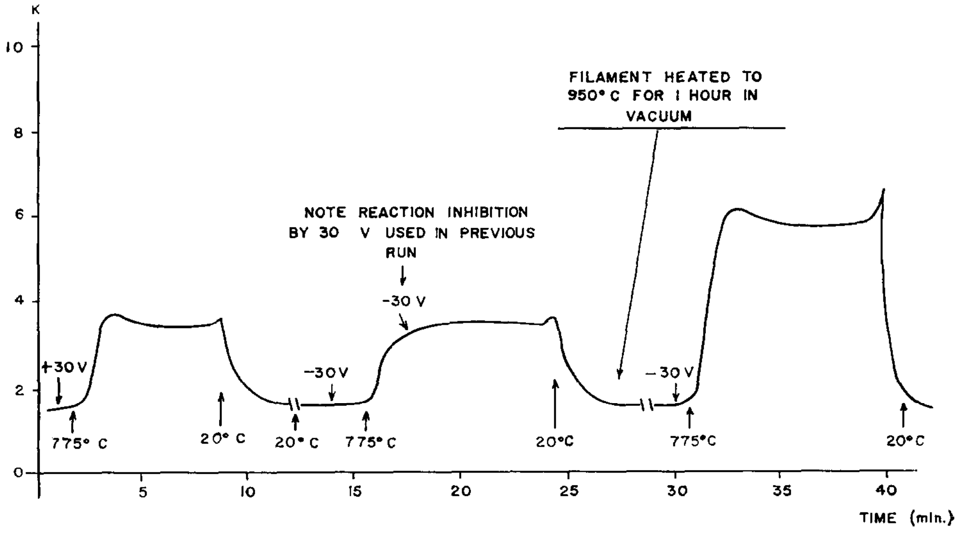

FIG. 7. Effect of previous exposure to positive voltage on catalysis of CO oxidation.

change in electron emission and rate of catalysis with electric fields indicates that catalysis can be partially controlled by external electric potentials.

The mechanism for these phenomena is not entirely clear at this time, but we have some speculative ideas based on analogies with other types of experiments. In particular we suggest that the large values of (K) and I_e observed during the induction period are due to mass migration of the catalyst material itself. Effects of this type are well known (*14, 15*) and catalysts are often observed to be grooved and twisted after long use.

The steady state exo-electron emission is proportionate to the rate of catalysis itself and may be due to the adsorption step in the reaction. Delchar (*4*) has reported the emission of exo-electrons during chemisorption of oxygen on nickel, but the emission rate decayed rapidly as the surface became saturated. We see a steady state level indicating continuous adsorption and desorption which would, of course, be necessary for a continuous catalytic reaction.

The surge observed when the catalyst is allowed to cool may be due to relaxation of the "active" surface state that exists during catalysis. Effects of this type have been observed by Moore (*16*) in silver thermal faceting experiments. The thermal facets developed at 865°C were observed to disappear as the target temperature was raised and to reappear as it was allowed to cool again. The extensive surface migration required to effect this change would induce copious exo-electron emission.

The fact that electric fields only affect catalysis if applied *before* the catalyst is heated, is somewhat surprising. Here we suggest that during the induction phase the catalyst surface is undergoing rearrangement to the state in which it is "active" for catalysis. During this period the surface arrangement can be affected by external electric fields. Effects of this type have been reported by Chopra (*17*) for thin films. In that study the electric field was applied *during* deposition and was shown to produce enhanced orientation of the deposited film. It may be significant that the electric field was *only* effective during deposition. If the field was applied to the completed film, no effect was noticed. We must emphasize that the parallelism here is not exact. The material used (*17*) was Ag or Au, and the field was in the plane of the film rather than perpendicular to it. This experiment is cited as an example of the effect of an electric field during the induction period when the film is moving toward an equilibrium configuration. Other suggestions of this "electric field effect on surface orientation" appear in the work of Little *et al.* (*18*) who showed that condensation of metal vapor from the gas phase was inhibited by the presence of intense electric fields.

Future studies of catalysis will involve following mass migration of the catalyst surface with an optical microscope using a soft X-ray system to monitor surface impurities.

APPENDIX

Another possible interpretation of the observed electron currents might be some gas phase ionization process similar to that observed by Umstead *et al.* (*19*). We disagree with this for several reasons:

1. In (*19*) only positive ions were observed and an attempt to detect electrons was not successful even at the 10^{-10} A level.
2. No ion current was observed by Umstead *et al.* (*19*) during catalytic combustion of CO or H_2. This suggests that the ionization they observed at pressures close to 1 atm was indeed due to gas phase reactions of complex molecules (their own explanation). This is in direct contrast to our results at 10^{-6} Torr with H_2 and CO.
3. After reading (*19*) we made several runs with a negatively biased collector to look for positive ions during the catalytic reaction. Typical results, for the oxidation of CO, are shown in Fig. 4. The positive ion current is just what one would expect from thermally induced desorption of sodium and potassium impurities from the platinum filament. Currents of this magnitude are observed when platinum, of this purity, is heated in vacuum.

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