

Observations of Exoelectron Emission Associated with Heterogeneous Catalysis¹

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INTRODUCTION

In an earlier paper (1) we discussed the observations of exoelectron emission associated with catalytic oxidation of CO, H₂, and NH₃ over a heated palladium wire. Other data on the NO, +NH₃ reaction over hot monel was reported in (2). In every case it was possible to monitor the rate of reaction and to determine activation energies from a measurement of the exoelectron current versus temperature.

All of the experiments discussed in (1) and (2) were performed in a vacuum system at some 10⁻⁵ Torr and the wire catalysts were heated by ac through an isolation transformer. Some readers raised the questions of: (a) Could this technique be used for observation of catalytic reactions at atmospheric pressure? (b) Were some of the observed effects due to the electrical current passing through the catalyst?

EXPERIMENTS AT 1 atm

To settle some of these questions we constructed the system shown in Fig. 1. The gas mixture was sampled upstream of the catalyst and again after the reaction had occurred. The exoelectron emission was collected by a stainless steel screen on the downstream side of the catalyst.

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We note that when electrons are emitted into a gas containing even a trace of oxygen, the electrons are immediately attached to oxygen molecules to form negative molecular ions (3). It is these ions that were collected in the experiment and all references to exoelectron current should be understood to refer to a current of negative molecular ions.

For these experiments the palladium wire catalyst (0.0254 cm diam) was supported on a ceramic tube into which a 100 W rod heater had been inserted. The palladium wire was electrically grounded to preclude the build-up of a charge but no electrical current was passed through the catalyst itself. Catalyst temperature was monitored by a small thermocouple just below the catalyst.

The reaction coefficient "K" was taken as the ratio of the CO₂ partial pressures at the inlet and outlet ends of the system. The numerical values of K are arbitrary because of changes in the mass spectrometer electron multiplier output with time and ambient gas pressure. The multiplier sensitivity remained effectively constant for a given run but changes over a period of weeks made it impractical to obtain an absolute value for the reaction coefficient.

To compare the exoelectron data to the reaction constants we plotted the exoelectron data in absolute terms, then the

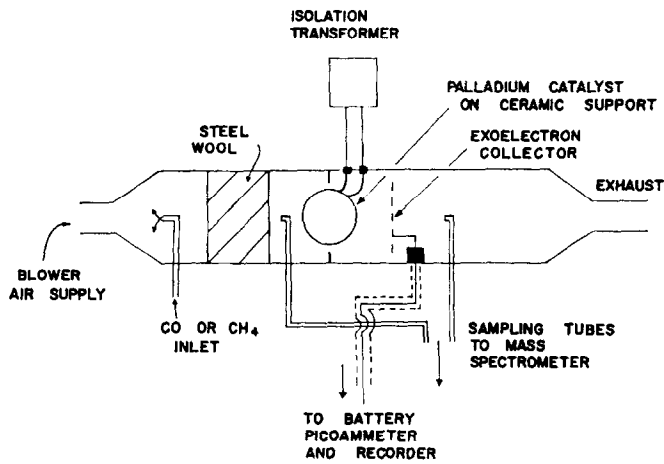


Fig. 1. Experimental system.

“arbitrary” values of K were plotted and moved vertically to bring the appropriate I_e and K curves to the same location. It was hoped that this would demonstrate that the I_e and K curves were parallel, for a given reactant to oxidizer mixture ratio.

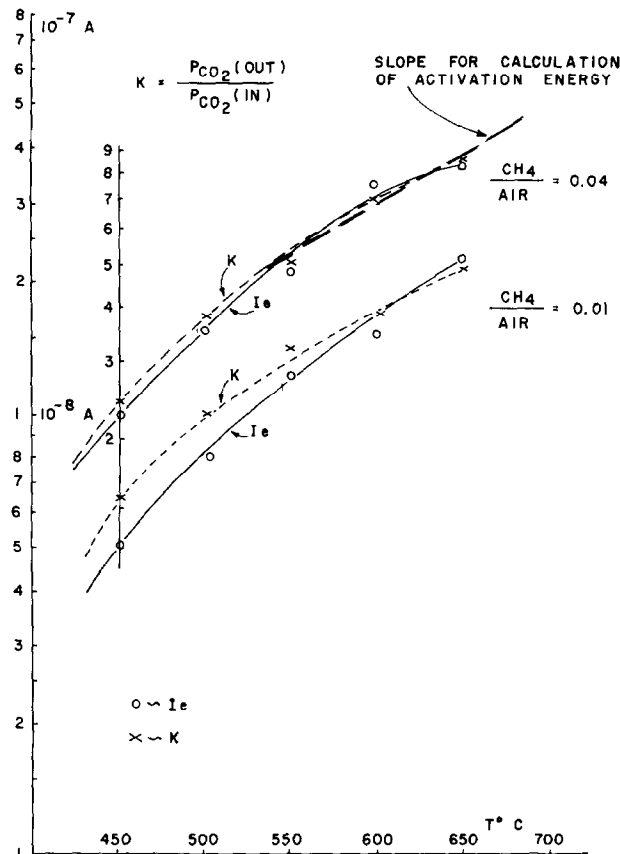


Fig. 2. Reaction constant (K) and exoelectron current (I_e) during catalytic oxidation of CH_4 .

This would in turn suggest that the exoelectron technique could be used for monitoring the rate of reaction.

RESULTS

The first experiments involved the oxidation of CH_4 with atmospheric air. The mixture ratio was held below 5% to preclude the hazard of explosion. Initial CH_4 experiments made use of natural gas, from El Paso Gas Co., with a charcoal trap to remove the mercaptans added as a signal of leaking gas. The results were erratic and the data reported below were obtained with "commercial" grade natural gas obtained from the Matheson Co. Mass spectrometric analysis indicated that the natural gas was some 93.6% CH_4 . The remainder was a mixture of ethane and propane.

Typical data for this reaction are plotted in Fig. 2 as I_e and K versus temperature for various CH_4 to air ratios. The 4% CH_4 I_e and K curves are essentially parallel suggesting that the electron current (I_e) could be used to monitor the rate of reaction. For 1% CH_4 there is some deviation of slope between the two curves; this may be due to the effect of adsorption on the metallic work function. In any case the difference is small at 600°C where a reaction of this type might be monitored.

Similar data for the CO oxidation reaction is shown in Fig. 3. Here commercial tank oxygen was used instead of air because of the lower heat of reaction. In Fig. 3 the 12% curves for I_e and K are essentially parallel. At 2% there is some deviation which we ascribe to thermally induced elec-

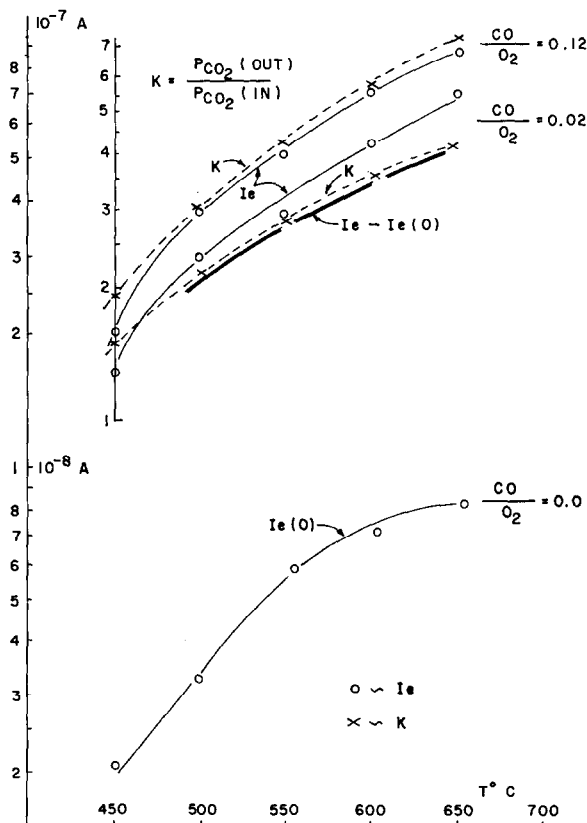


FIG. 3. Reaction constant (K) and exoelectron current (I_e) during catalytic oxidation of CO.

tron emission. The results of a 0% (CO) level run are shown in Fig. 3. If the numerical values from the 0% curve are subtracted from the 2% I_e curve the resultant $I_e - I_e(0)$ values are essentially parallel to the 2% K curve. Once again we suggest that the electron emission current is a convenient way to monitor to catalytic reaction.

DISCUSSION

The mechanism relating catalysis to exoelectron emission is by no means clear. We suggest that electron emission is triggered by the adsorption-desorption cycle. Delchar (4) has reported electron emission associated with the adsorption of oxygen on nickel; if emission is due to adsorption the continuous adsorption-desorption cycle of catalysis would generate a steady current of electrons at a rate proportionate to the rate of reaction.

A somewhat similar mechanism is the "churning" of the surface reported by Czanderna (5). This gross surface motion was associated by the author with oxygen adsorption and would effectively decrease the metallic work function thereby increasing the rate of electron emission.

The data of Figs. 2 and 3 permit a calculation of the activation energy (E) of the reactions. In the case of Fig. 2 a straight line was drawn parallel to the 4% curves and the I_e and K values were used to calculate " E ." In all cases the formulas used were taken from Ref. (1) in the form

$$\frac{I_{e1}}{I_{e2}} \text{ or } \frac{K_1}{K_2} = \exp \frac{-E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

The results for the CH_4 reaction, Fig. 2, were 7.8 and 7.7 kcal/mole. For Fig. 3, the CO reaction, the values were 7.8 and 7.0 kcal/mole.

These data can be compared with those of Anderson *et al.* (6) taken on a palladium catalyst supported on alumina. Activation energy values of 21.8 kcal/mole were observed in the 300–450°C temperature range. The CH_4 data may be compared with those of Bonzel and Ku (7) and the work of Palmer and Smith (8), both of which were done with platinum rather than palladium catalysts. Bonzel and Ku reported an activation energy of 2.9 kcal/mole while Palmer and Smith obtained a value of 20 kcal/mole. The very large differences between these two results may have been due to the difference in experimental conditions; they are evidence of the problem of obtaining reliable activation energy data for these reactions.

CONCLUSIONS

We suggest that the exoelectron emission from the catalyst may be used to monitor the rate of oxidation of CO and CH_4 over palladium catalysts. Indirect heating of the catalyst and atmospheric pressure have no effect upon this monitoring system.

REFERENCES

1. Hoenig, S. A., and Tamjidi, F., *J. Catal.* **28**, 200 (1973).
2. Hoenig, S. A., and Tamjidi, F., *Automot. Eng.* **81**, 68, 69 (1973).
3. Geballe, R., and Harrison, M. A., *Phys. Rev.* **85**, 372, 373 (1952).
4. Delchar, T. A., *J. Appl. Phys.* **38**, 243 (1967).
5. Czanderna, A. W., *J. Phys. Chem.* **70**, 2120 (1966).
6. Anderson, R. B., Stein, K. C., Feenan, J. J., and Hofer, L. J. E., *Ind. Eng. Chem.* **53**, 809 (1961).
7. Bonzel, H. P., and Ku, R., *Surface Sci.* **33**, 91 (1972).
8. Palmer, R. L., and Smith, J. N., *J. Chem. Phys.* **60**, 1453 (1974).