JOURNAL OF CATALYSIS 24, 224-232 (1972)

Chemically Stimulated Exo-electron Emission from Silver Catalyst during Partial Oxidation of Ethylene

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Received February 9, 1971

Exo-electron emission from a silver catalyst during partial oxidation of ethylene has been studied by measuring simultaneously the exo-electron emission rate and the rate of ethylene oxide formation. The silver catalyst emits exo-electron continuously in a temperature range 150–210°C and its emission rate is proportional to the rate of ethylene oxide formation. The temperature dependence of the exo-electron emission obeys the Richardson relation for thermo-electron emission from semiconductor, whereas the rate of ethylene oxide formation fits to the Arrhenius equation.

This continuous exo-electron emission is discussed using a schematic diagram of electronic levels of the silver surface with conclusions that the exo-electron emission from the silver catalyst during partial oxidation of ethylene is regarded as a thermo-electron emission from a thin semiconducting oxide layer on silver, the work function of which is reduced by adsorption of ethylene in the form of ethylene oxide. No exo-electron emission and no ethylene oxide formation are shown to occur from metallic copper, nickel oxide and iron oxide, with which only complete oxidation of ethylene proceeds.

INTRODUCTION

It is known that the exo-electron emission, vaporization of very low energy electrons from solids, can be produced in a variety of ways, abrasion (*1*), mechanical deformation (*2*), irradiation by energy particles (*3, 4*), light illumination (*5, 6*), and chemical reaction (*7, 8*). The exo-electron emission in most cases is sensitive to structural defects of the surface and bulk of the solids, and thereupon it has been applied to studying the surface of metals (*9*), the electronic level in luminescent solids (*10, 11*), and the activity of solid catalysts (*12*).

In the field of catalyst a few investigations on the relation between the exo-electron emission and catalytic activities have been made for silver (*12–14*), zinc oxide (*15*), and ferric oxide (*16*): In these studies the exo-electron emission and the catalytic activity were measured separately.

The chemically stimulated exo-electron emission has been found by Lohff (*8*) to occur with the oxidation of zinc, and by Seidl (*7*) with the oxidation of copper. Recently, Nassenstein and Menold (*12*) found using a Geiger–Müller tube that an exo-electron emission takes place at 200–400°C from silver catalysts which have once been subjected to the partial oxidation of ethylene. This fact was confirmed in our laboratory with an additional result (*13*) that the emission activity is proportional to the catalytic activity. We (*14*) also found by making simultaneous measurements of the exo-electron emission and the ethylene oxide formation that a chemically stimulated exo-electron emission occurs continuously from a silver catalyst during partial oxidation of ethylene.

This paper describes the continuous exo-electron emission from a silver catalyst and confirms the relationship between the exo-electron emission and the rate of ethylene oxide formation. Furthermore, metallic copper, nickel oxide and iron oxide are examined for exo-electron emission and catalytic activity during oxidation of ethylene.

EXPERIMENTAL

Figure 1 shows the block diagram of the apparatus used, which consisted of a Geiger–Müller tube with a fine tungsten wire anode and a stainless-steel tube cathode; the stainless steel was used because it was catalytically inert to ethylene oxidation. The center of the tube had an aperture at the center of tube wall that opened directly into a quartz reaction compartment, in which the sample catalyst 5 g in weight could be heated from below by a small external furnace. The G–M tube was always kept at room temperature with a cooling water jacket, and the temperature of the sample was controlled programmatically.

The gas mixture, 91.8% argon, 3.4% ethylene, and 4.8% oxygen, was used for the reaction gas of ethylene oxidation. This gas mixture also worked fairly stably as a quenching gas in the G–M tube at an anode potential 2,100 V even with the sample heated in the temperature range to be examined, provided that decrease in ethylene concentration during measurement was small. The background count of the G–M tube was about 100 counts/min at the sample temperature lower than 400°C. The counting yield of the G–M tube was measured using a radioactive phosphate whose emission activity had been estimated by a 2π-counter. Table 1 shows the counting yield of the G–M tube at different radioactive phosphate temperatures.

The gas mixture was allowed to flow at a constant speed through the counter tube and the reaction compartment. The rate of ethylene oxide formation was measured by a high-sensitive gas chromatograph while the measurement of the exo-electron emission was being made.

The silver catalyst was prepared after Hirasa and Hirayama (*17*): An alkaline solution (36.5 g KOH in 30 ml water) was slowly added to a $AgNO_3$ solution (27.3 g $AgNO_3$ in 300 ml water) at 10°C. After precipitation of silver (I) oxide, 12.5 ml of 30% HCHO solution was added to the solution, which was then kept for 30 min then boiled for 1 hr. The precipitate was then filtered, washed with distilled water, treated with 2% HNO_3 solution for 2 or 3 min, and washed again with distilled water until no nitrate ions were detected. This precipitate was finally dried at 80°C before experiments.

Iron oxide ($Fe_3O_4 \cdot nH_2O$) was prepared by precipitation using $FeSO_4$, $Fe_2(SO_4)_3$ and NaOH solutions. Copper metal powder and nickel oxide ($Ni_2O_3 \cdot nH_2O$) were of commercial grade.

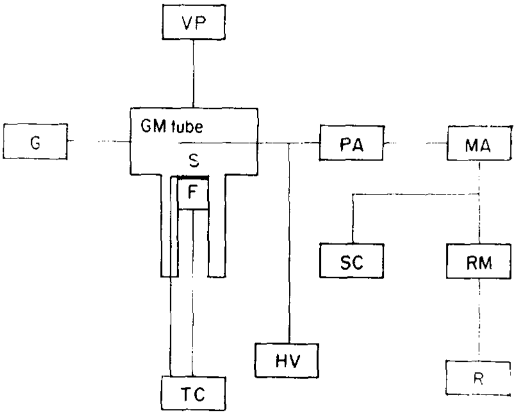

FIG. 1. Block diagram of apparatus for measurement of exo-electron emission. F: Furnace. VP-Vacuum Pump. G: Gas. S: Sample. TC: Thermocouple. HV: High Voltage Supply. SC: Scaler. PA: Pre-amp. MA: Main Amp. RM: Rate Meter. R: Recorder.

TABLE 1
RELATION BETWEEN COUNTING YIELD OF G-M TUBE AND RADIOACTIVE PHOSPHATE TEMPERATURE

Temperature (°C)	Counting yield (%)
20	32
100	39
150	44
200	49
250	53
300	58

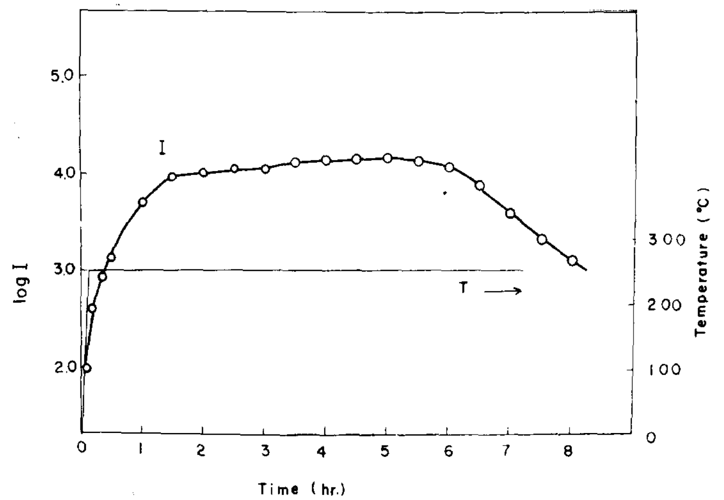

FIG. 2. Time variation of the rate of exo-electron emission from a silver catalyst during partial oxidation of ethylene at 250°C; the exo-electron emission rate, *I* (counts/min), in the ordinate includes the background counts. Catalyst temperature is shown in right-hand ordinate.

RESULTS

Continuous Emission of Exo-electrons

Figure 2 shows the change in the rate of exo-electron emission from the silver catalyst during partial oxidation of ethylene at 250°C. Also shown is the catalyst temperature. The exo-electron emission is seen to occur continuously for an extended period of hours.

Figure 3 shows also the rate of exo-electron emission from the silver catalyst at 250°C in the absence and presence of oxygen in the flowing gas. In the absence of oxygen the measured count rate was of the background level, indicating no exo-electron emission occurred. When oxygen was introduced into the gas, its composition was then 91.8% argon, 3.4% ethylene and 4.8% oxygen, a rapid increase in the counting rate was observed reaching a steady rate at which the emission con-

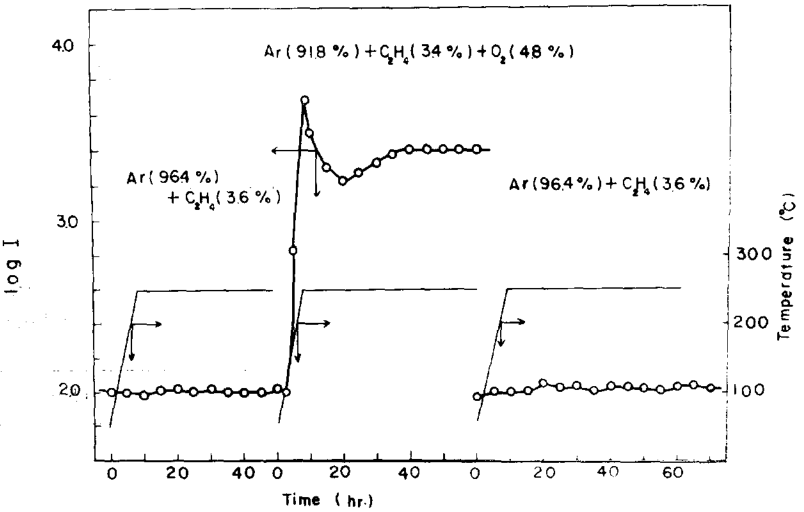

FIG. 3. Time variation of the rate of exo-electron emission from a silver catalyst at 250°C in the absence and presence of oxygen in the flowing gas; the exo-electron emission rate (counts/min) in the ordinate includes the back ground counts.

tinued as long as the composition of the flowing gas was kept constant. At the same time, formation of ethylene oxide was detected by gas chromatography, indicating that partial oxidation of ethylene was taking place on the silver catalyst. Removal of oxygen from the gas resulted in again no exo-electron emission and no ethylene oxide formation. From these experiments it is evident that the presence of oxygen in the gas is essential for the exo-electron emission to occur as well as for partial oxidation of ethylene on a silver catalyst.

Figure 4 shows the effect of temperature on the emission rate of exo-electron and on the formation rate of ethylene oxide, for which the temperature of the silver catalyst was raised step-wise from 25°C to 210°C followed by a descent to 25°C. Simultaneous measurements of the rate of the exo-electron emission and the formation of ethylene oxide at each level of temperature were made as a function of time. With the aid of the counting efficiency of the G–M tube shown in Table 1, it was estimated that one exo-electron was emitted with production of 2×10^{14} molecules of ethylene oxide at 200°C.

Temperature Dependence

From the measured count rates shown in Fig. 4 and the counting yield of the G–M tube shown in Table 1, we can estimate the true emission rate of exo-electrons as a function of temperature. Figure 5 shows the Arrhenius plot for the rate of ethylene oxide formation and the Richardson plot for the rate of exo-electron emission assuming thermo-electron emission from a semiconductor. The apparent activation energy for the formation of ethylene oxide is estimated to be 14.2 kcal/mole (0.62 eV), and the apparent energy required for the exo-electron emission to be 18.7 kcal/mole (0.8 eV).

Exo-electron Emission from Copper, Nickel Oxide, and Iron Oxide

Copper, nickel oxide, and iron oxide were used as catalysts instead of silver, and the same measurements as above were made using the gas of the same composition. With these catalysts, no exo-electron

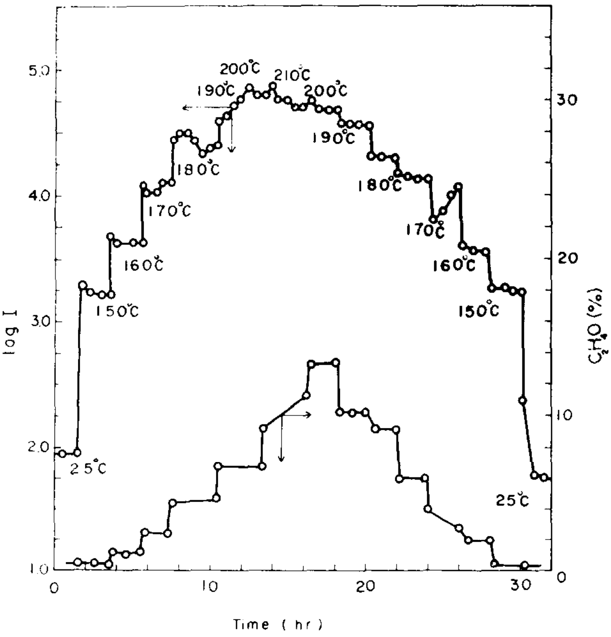

FIG. 4. Effect of temperature on the rate of exo-electron emission and on the formation rate of ethylene oxide in the temperature range from 25° to 210°C; the exo-electron emission rate in the ordinate includes the background counts.

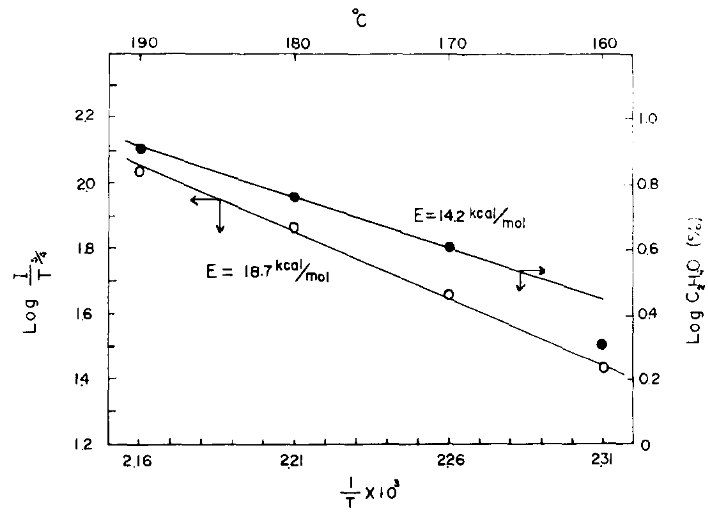

FIG. 5. Richardson plot of exo-electron emission and Arrhenius plot of ethylene oxide formation; the background counts are substracted for the exo-electron emission rate.

emission and no ethylene oxide formation were observed, and only the reaction taking place was complete oxidation of ethylene to CO_2 and H_2O. Figure 6 shows a time variation of the counting rate for a copper powder catalyst during oxidation of ethylene at 320°C. The counting rate is seen to be at the background level.

DISCUSSION

Exo-electron emission previously reported in the literature are all temporary phenomena and last for a limited number of exo-electrons depending on the kind and extent of pre-excitation which the solids have received.

Our experiment, however, demonstrates that a continuous exo-electron emission occurs, without any pre-excitation, from the surface of silver on which partial oxidation of ethylene is taking place. This continuous exo-electron emission suggests that the partial oxidation of ethylene on the silver catalyst causes chemical excita-

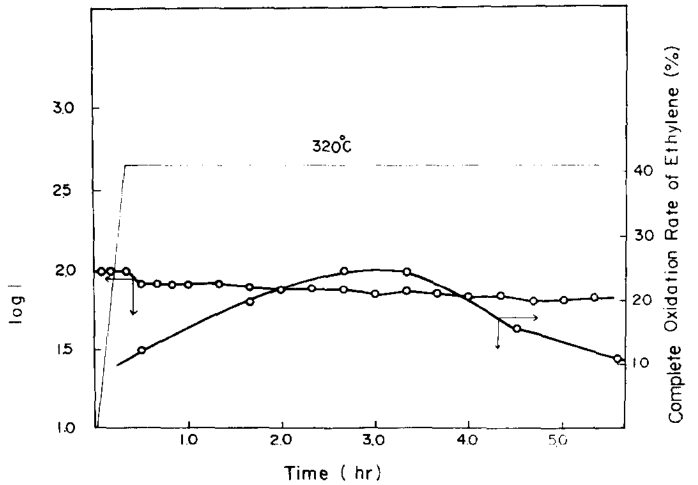

FIG. 6. Time variation of the counting rate and of the complete oxidation rate of ethylene for metallic copper at a reaction temperature of 320°C; the counting rate is equal to the background counts.

tion of the silver catalyst with energy enough for electrons to vaporize from its surface.

There have been in literature two different approaches to the mechanism of exo-electron emission from solids. One is based on the fact that for ionic crystals the exo-electron emission activity is related to the concentration of lattice defects such as color centers *(18, 19)* and luminescence centers *(20)*, and assumes that the exo-electron comes from donor levels associated with lattice defects *(33)*. The other, which is based on the fact that the exo-electron emission from metals in vacuum is markedly affected by the presence of residual gas *(21)*, emphasizes the role of gas adsorption on the metal surface, and assumes a decrease of the work function *(22–25)* or creation of a high electric field *(26)* at the surface.

The work function of silver has been observed by Kummer *(28)* to increase by 0.2 eV when silver adsorbs oxygen at 200°C. Lilov *(29)*, however, has found that the work function of silver may increase or decrease depending on the temperature and the oxygen pressure, and ascribed a decrease in the work function to the penetration of adsorbed oxygen into the surface layer of silver. The oxygen penetrating into the surface layer would form a silver oxide, probably nonstoichiometric silver oxide with lattice defects, which may trap excess electrons, as suggested by Feller–Kniepmeier *(30)*.

Our previous report *(27)* has shown that adsorption of oxygen on silver results in formation of Ag_2O with molecular oxygen ion, O_2^-, adsorbed on it even at temperatures higher than 190°C at which bulk Ag_2O is thermodynamically unstable. Ethylene is known to adsorb on oxygenated silver as an electron donor *(31)*.

If we assume here that ethylene adsorbs on nonstoichiometric silver oxide in the form of ethylene oxide with a fractional plus charge orienting out of the silver surface, then a reduction of the work function of oxygenated silver would be expected to occur in the presence of adsorbed ethylene because of its dipole alignment, which would contribute to the emission of electrons from the defective silver oxide where electrons are trapped.

Exo-electron emission from a silver catalyst during partial oxidation of ethylene may now be interpreted as follows: During partial oxidation of ethylene the silver surface is simultaneously oxidized by oxygen and then reduced by ethylene. This means that during the reaction the formation and decomposition of the silver oxide containing excess electrons takes place at the same time. The excess electrons trapped in the oxide can be emitted by assuming that the adsorption of ethylene which forms ethylene oxide lowers the work function. The continuous emission of electrons would occur as long as the oxide layer is renewed continuously. The mechanism of catalytic oxidation of ethylene on silver has not yet been made clear. However, it has been suggested *(32–35)* that the adsorbed molecular oxygen contributes to the formation of ethylene oxide and that the complete oxidation proceeds through the adsorbed ionic oxygen. This mechanism seems to be widely accepted at present. Based on this mechanism, we present in Fig. 7 a schematic diagram for the electronic level of the silver surface in terms of the band model of a semiconducting oxide layer.

It can be seen in Fig. 7 that adsorption of ethylene on the oxygenated silver surface results in a reduction of the energy barrier from E_a to E_b so that electrons can jump from the Fermi-level into the conduction band at the surface. Since E_a is larger than E_b, Φ_a, the work function of the $Ag–O_2$ system, is larger than Φ_b, the work function of the $Ag–O_2–C_2H_4$ system. It may therefore be concluded that the exo-electron emission from a silver catalyst during partial oxidation of ethylene is a thermo-electron emission from a thin semiconducting oxide layer formed on silver, the work function of which is lowered by adsorption of ethylene in the form of ethylene oxide.

Thermo-electron emission from a semiconductor can be given by the following Richardson equation.

$$\left.\begin{aligned} j &= \bar{D}n^{1/2}AT^{5/4}\exp(-\Phi_b/kT)\\ \Phi_b &= E_b+\chi\\ A &= e\left\{\frac{(2\pi)^{1/2}k^{5/2}m^{1/2}}{h^3}\right\}^{1/2}\end{aligned}\right\} \qquad (1)$$

where j is the emission rate per unit area of the semiconductor on the oxygenated silver surface, $\bar{D}$ the mean transmittivity of electron, n the number of electron in the conduction band, m the effective mass of the electron in the conduction band, and Φ_b the work function of the semiconductor. If the exo-electron emission from a silver catalyst is a thermo-electron emission from a thin semiconducting oxide layer formed on silver, the exo-electron emission rate, J, can be given by the following equation.

$$J = \theta j,\ \theta = \theta_0\exp(-Q/kT) \qquad (2)$$

where θ is the fractional coverage of the silver surface by the semiconducting oxide, Q the heat of formation of the semiconducting oxide, and θ_0 a constant. By substituting equation (1) into equation (2), we obtain

$$J = \bar{D}n^{1/2}AT^{5/4}\theta_0\exp\left(-\frac{Q+E_b+\chi}{kT}\right) \qquad (3)$$

Since the relation between log $J/T^{5/4}$ and $1/T$ in Eq. (3) is linear, $(Q+E_b+\chi)$ can be estimated from the slope of the straight line obtained in Fig. 5. Thus we estimate $(Q+E_b+\chi) = 18.7$ kcal/mole (0.81 eV).

The formation rate of ethylene oxide,

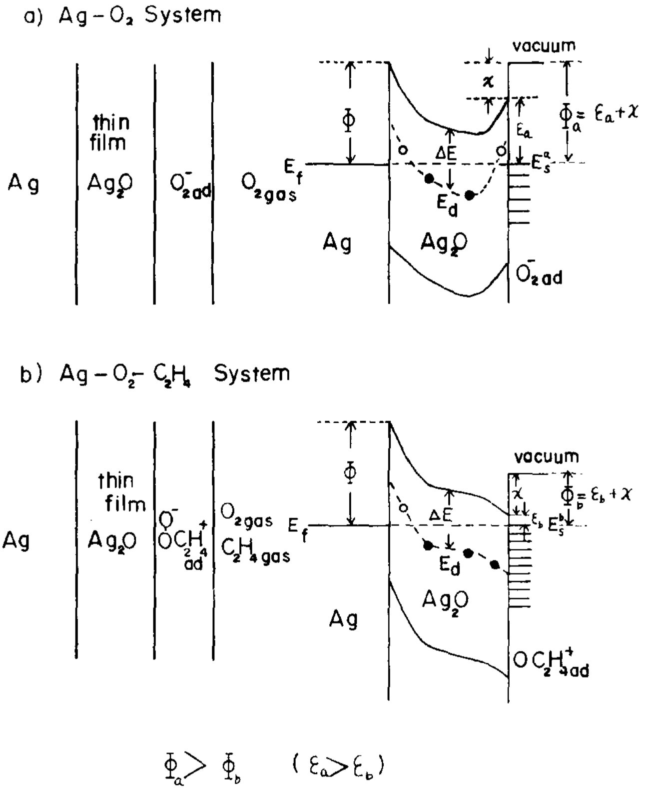

FIG. 7. Schematic diagram for the electronic level of silver surface in terms of the band model of semiconducting oxide layer. Φ, work function of silver. χ, electron affinity of a thin silver oxide. Φ_a, work function of a thin silver oxide in Ag–O_2 system. Φ_b, work function of a thin silver oxide in Ag–O_2–C_2H_4 system. $E_s{}^a$, surface level of silver oxide in Ag–O_2 system produced by adsorbed oxygen. E_a, energy difference between $E_s{}^a$ and the bottom of the conduction band at the surface. $E_s{}^b$, surface level of silver oxide in Ag–O_2–C_2H_4 system produced by adsorbed ethylene in the form of ethylene oxide. E_b, energy difference between $E_s{}^b$ and the bottom of the conduction band at the surface. ΔE, energy difference between the conduction band and the donor level of silver oxide. E_f, Fermi level of silver oxide. E_d, donor level of silver oxide.

$V_{C_2H_4O}$ can be given by the following equations

$$V_{C_2H_4O} = \alpha M \tag{4}$$

$$M = \beta\theta \tag{5}$$

$$\beta = \beta_0 \exp(-Q'/kT) \tag{6}$$

where, α is the proportionality constant, M the amount of adsorbed ethylene oxide on nonstoichiometric silver oxide, Q' the adsorption heat[*] of ethylene oxide, and β_0 a constant. By substituting Eqs. (2), (5) and (6) into (4), we obtain

$$V_{C_2H_4O} = \alpha\beta_0\theta_0 \exp[-(Q + Q')/kT] \tag{7}$$

From the linear relation between formation rate of ethylene oxide and $1/T$ shown in Fig. 5, $(Q + Q')$ is estimated to be 14.2 kcal/mole (0.62 eV).

In our previous report (*36*) for ethylene adsorption on oxygenated silver, we have estimated that the amount of adsorbed ethylene is small and the heat of ethylene adsorption during oxidation of ethylene is about 3.5 kcal/mole. Therefore, we consider that ethylene adsorbs on oxygenated silver in the form of ethylene oxide, and then Q' is expected to be about 3.5 kcal/mole (0.15 eV). Hence, Q is 10.7 kcal/mole (0.47 eV) and $(E_b + \chi)$ 8.0 kcal/mole (0.35 eV). Also if we assume that the electron affinity, χ, of the nonstoichiometric silver oxide is not so different from that of BaO with $\chi = 0.3$ eV (*37*), E_b is estimated to be nearly zero. This implies that the Fermi level of the thin silver oxide with adsorbed ethylene would be equal to the level of the bottom of the conduction band at the surface.

SUMMARY

A chemically stimulated exo-electron emission occurs continuously from silver catalyst during partial oxidation of ethylene, and the emission rate of exo-electron is proportional to the rate of ethylene oxide formation. No exo-electron emission occurs from metallic copper, nickel oxide and iron oxide in ethylene–oxygen mixture, all of which has no catalytic activity for ethylene oxide formation but for complete oxidation of ethylene.

This exo-electron emission from silver catalyst during partial oxidation of ethylene is interpreted as a thermo-electron emission from a thin semiconducting oxide on silver, the work function of which is lowered by adsorption of ethylene in the form of ethylene oxide. The energy required for the formation of the thin semiconducting oxide and its work function are estimated to be 10.7 kcal/mole (0.47 eV) and 8.0 kcal/mole (0.35 eV), respectively.

ACKNOWLEDGMENTS

The authors wish to thank Lecturer K. Kudo of our laboratory for valuable suggestions to experimental apparatus and H. Mashima for assistance in conducting experimentals.

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[*] Q' corresponds to the heat of adsorption only when the coverage of adsorbed ethylene oxide is small.

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