

Solid-Electrolyte-Aided Study Of Methane Oxidation on Polycrystalline Silver

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The oxidation of methane on porous polycrystalline Ag films supported on yttria-stabilized zirconia was studied in a CSTR at temperatures between 450 and 600°C and atmospheric total pressure. The technique of solid-electrolyte-potentiometry (SEP) was used to monitor the chemical potential of oxygen adsorbed on the catalyst. The kinetic and potentiometric results are consistent with an Eley-Rideal reaction model with adsorbed atomic oxygen reacting with gaseous methane. The rate of CH₄ combustion was found to satisfy $r = K_R P_{\text{CH}_4} \cdot K_O a_O / (1 + K_O a_O)$ with $K_R = 1.97 \exp(-10,300/T)$ mol/s · bar and $K_O = 7.56 \times 10^{-5} \exp(8500/T)$ bar^{-1/2} on a porous film that could adsorb a total of 2.5×10^{-6} moles O₂. The steady state atomic oxygen activity satisfies the equation $P_{\text{O}_2}^{1/2}/a_O - 1 = K_R P_{\text{CH}_4}/K_D$ with $K_D = 0.172 \exp(-9500/T)$ g atom O/s. A simple mechanism is proposed which explains all the experimental observations.

INTRODUCTION

The heterogeneous oxidation of methane usually results in its complete conversion to carbon dioxide and water. Small amounts of formaldehyde, methanol, and formic acid have been identified (1, 2). Formaldehyde has also been reported to be the intermediate product of homogeneous methane oxidation (3). Thus formaldehyde is considered to be the main intermediate formed during the oxidation of methane but selectivities to that product are very low, probably because formaldehyde when formed undergoes fast decomposition and oxidation reactions (4, 5).

Nevertheless, since direct formation of formaldehyde from methane would be financially preferable compared to the usual industrial routes (4), various workers have investigated the nature and role of intermediate products in an effort to isolate appreciable quantities of such compounds (6-14). Catalysts such as Pd and Ag have been reported to give best results concerning selectivities to oxygenated products (6, 9-11). Firth studied the kinetics of methane

oxidation on Pd-Au alloys as well as the effect of methane on methanol oxidation (7). Cullis *et al.* studied the oxidation of CH₄ on Pd catalysts and the effect of halogen compounds on the yield and the selectivity to formaldehyde (6). Mann and Dosi examined the above reaction over Pd-supported on Al₂O₃ (10). Both groups of investigators report a substantial increase of the selectivity to formaldehyde when halogen modifiers are introduced in the reactor although the yield decreases to some extent (6, 10).

It has been recently found that electrochemical oxygen "pumping" increases considerably the yield and the selectivity to ethylene oxide during ethylene oxidation over silver catalysts (15, 16). On the basis of this idea an attempt is made to increase the selectivity to oxygenated products during methane oxidation by using the above electrochemical technique (17). Despite its simplicity and technical interest only a few investigators (9, 13) have studied the Ag-catalyzed oxidation of methane and the reaction mechanism is unknown. A detailed kinetic study of the above reaction is the

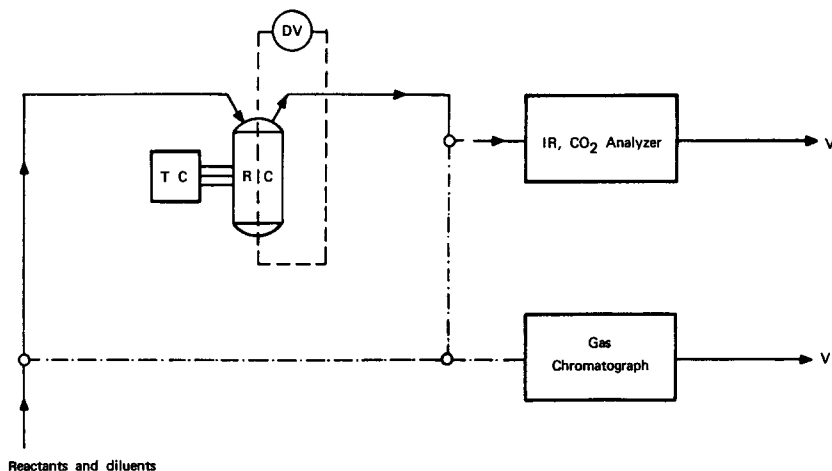


FIG. 1. Schematic diagram of apparatus. RC, reactor cell; TC, temperature controller; DV, differential voltmeter; V, vent.

subject of the present communication. Kinetics are combined with *in situ* electrochemical measurement of the activity of oxygen adsorbed on the catalyst surface using the technique of solid electrolyte potentiometry (SEP). The technique has already been used in conjunction with kinetic measurements in order to study the mechanism of various catalytic oxidations (18–21). Reactor cells similar to the one used in this study have been used so far (a) in order to enhance the rate of NO decomposition (22), ethylene oxidation (16), and CO hydrogenation (23) on metal catalysts; (b) as fuel cells (24); and (c) as a means of co-generating electricity and useful chemicals (25).

EXPERIMENTAL METHODS

A schematic diagram of the apparatus used for the kinetic and potentiometric studies is shown in Fig. 1. The reactor is a stabilized zirconia tube (8% Y_2O_3 -stabilized ZrO_2) shown in Fig. 2. The reactor volume was 30 cm³. Over the flow rates employed in the present study it has been shown (26) that the reactor is well mixed (CSTR).

The silver catalyst film was deposited on the flat bottom of the zirconia tube using an Ag emulsion in butyl acetate obtained from G.C. Electronics. A few drops of the

silver suspension were deposited on the flat bottom of the tube (Fig. 2) followed by drying and calcining in air at 600°C for 4 h. The catalyst preparation was identical to that followed during the study of ethylene oxidation. AES and SEM spectra have already

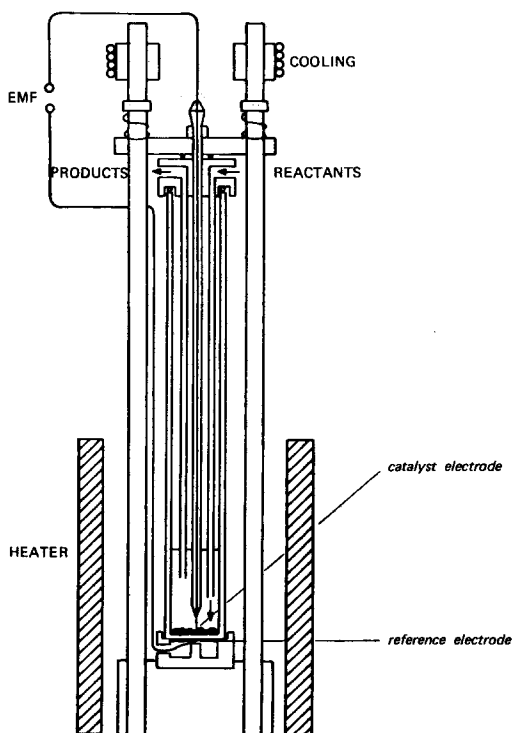


FIG. 2. Reactor cell configuration.

been presented in previous communications (18, 26). A similar Ag film was deposited on the outside wall of the zirconia tube. This Ag film was exposed to air and served as the reference electrode.

The silver catalyst film could adsorb approximately 2.5×10^{-6} mol of O_2 . The superficial surface area of the film was 2 cm^2 and the true active surface area of the catalyst was approximately 2400 cm^2 and was measured with the method of ethylene titration as it has been described in detail elsewhere (26).

An appropriately machined stainless-steel cap was clamped to the open end of the zirconia tube (Fig. 2). The cap had provision for introduction of reactants, removal of products, as well as for introduction of a Ag wire, partly enclosed in a Pyrex tube, to make contact with the internal Ag film catalyst electrode. A similar silver wire was in contact with the outside electrode and the two wires were connected through a Fluke 8600A millivoltmeter. The reactor temperature was controlled within 2°C by using a Omega Model 49 temperature controller.

The reactants were AIRCO CH_4 certified diluted in N_2 and Zero grade air. They could be further diluted with N_2 . Calibrated flowmeters were used to measure the total flow rate. A dual column Perkin-Elmer Sigma 3B gas chromatograph with a TC detector was used to analyze on-line reactants and products. A Poropak Q column separated CO_2 , H_2O , and air and a molecular sieve 5A column separated N_2 , O_2 , and CH_4 at room temperature. The concentration of CO_2 in the effluent stream was also monitored by means of an Infrared Industries Model 703D infrared CO_2 analyzer. At steady state the CO_2 concentration as measured by the ir analyzer was in very good agreement (within 3%) with the GC measurement.

Measurement of the Oxygen Activity

The thermodynamic activity of oxygen on the Ag catalyst was measured *in situ*

with the technique of solid electrolyte potentiometry (SEP). The above technique originally proposed by Wagner (27) has been used so far in a number of kinetic studies (18-21). It has been well established (18, 27) that the measured open-circuit emf reflects the difference in chemical potential of oxygen adsorbed on the two silver electrodes:

$$E = \frac{1}{4F} [\mu_{O_2}(\text{Ag, catalyst}) - \mu_{O_2}(\text{Ag, reference})], \quad (1)$$

where F is the Faraday constant and E the measured open-circuit emf. The chemical potential of oxygen adsorbed on the reference electrode which is in contact with air ($P_{O_2} \approx 0.21 \text{ bar}$) is given by

$$\begin{aligned} \mu_{O_2}(\text{Ag, reference}) \\ = \mu_{O_2}^0(\text{g}) + RT \ln (0.21), \quad (2) \end{aligned}$$

where $\mu_{O_2}^0(\text{g})$ is the standard chemical potential of oxygen at the temperature of interest. The activity a_0 of adsorbed oxygen can be defined from the equation

$$\mu_{O_2}(\text{catalyst}) = \mu_{O_2}^0(\text{g}) + RT \ln a_0^2. \quad (3)$$

Thus a_0^2 expresses the partial pressure of gaseous oxygen that would be in equilibrium with oxygen adsorbed on the silver surface, if such an equilibrium were established. Therefore combining Eqs. (1), (2), and (3) one obtains

$$a_0 = (0.21)^{1/2} \exp\left(\frac{2FE}{RT}\right). \quad (4)$$

The above equation permits direct calculation of the surface oxygen activity by simply measuring the temperature and the open-circuit emf of the cell. When thermodynamic equilibrium exists between surface and gaseous oxygen

$$a_0 = P_{O_2}^{1/2}. \quad (5)$$

Obviously when no reaction occurs Eq. (5) should be satisfied. Thus the correct performance of the cell was verified by introducing in the reactor O_2 - N_2 mixtures of known

compositions and obtaining agreement within 1 and 2 mV with the Nernst equation

$$E = \frac{RT}{2F} \ln \left(\frac{P_{O_2}}{0.21} \right)^{1/2} \quad (6)$$

RESULTS

Kinetic Measurements

The kinetics were studied at temperatures between 450 and 600°C, methane partial pressures between 10^{-2} and 7×10^{-2} bar and oxygen partial pressures between $.4 \times 10^{-2}$ and 14×10^{-2} bar. The total pressure of the mixture was 1 bar. Nitrogen was used as a diluent. By varying the partial pressure of nitrogen we could maintain either P_{CH_4} or P_{O_2} at a desired level.

The possibility of homogeneous methane oxidation was investigated by using a zirconia tube identical to that used as a reactor but without depositing catalyst on its bottom. Methane and oxygen were passed through the "blank" reactor at flow rates and compositions similar to those employed in the kinetic study. No measurable reaction rate was observed below 550°C and at 600°C the rate of CH_4 consumption was 2 orders of magnitude lower than the rate obtained catalytically (28). Thus problems of homogeneous reaction were small enough to be neglected.

The catalyst activity remained constant within 2 and 3% for at least 4 weeks after an initial induction period which lasted approximately 48 h. All the data reported below were obtained after the termination of the induction period.

In all the range of temperatures and gas compositions examined, only CO_2 and H_2O were observed as products at measurable quantities. Trace amounts of formaldehyde were observed in two cases at 600°C. The concentrations of formaldehyde detected were very low (<3% of CO_2 produced).

It can thus be concluded that at least in absence of halogen modifiers silver catalyzes the oxidation of CH_4 to the products of complete oxidation, CO_2 and H_2O .

The absence of external diffusional ef-

fects was verified by varying the total flow rate of constant gas composition and observing negligible change on the reaction rate. Internal diffusional limitations were also absent. This was verified by varying the film thickness of the porous Ag catalyst and observing no change (<2%) in the surface oxygen activity for the same temperature and gas composition. Since the oxygen activity is measured at the gas-metal zirconia interline and is a function of gas composition, this proves absence of diffusional effects inside the catalyst pores (18, 26).

The reaction rate r (moles of methane consumed/s) was calculated from the raw kinetic data of the CSTR using the appropriate mass balance

$$r = GX_{CO_2}, \quad (7)$$

where X_{CO_2} is the mole fraction of CO_2 in the effluent stream and G is the total molar flow rate. The following figures contain kinetic and potentiometric results of this study.

The rate of CO_2 formation is plotted in Fig. 3 vs the partial pressure of methane in

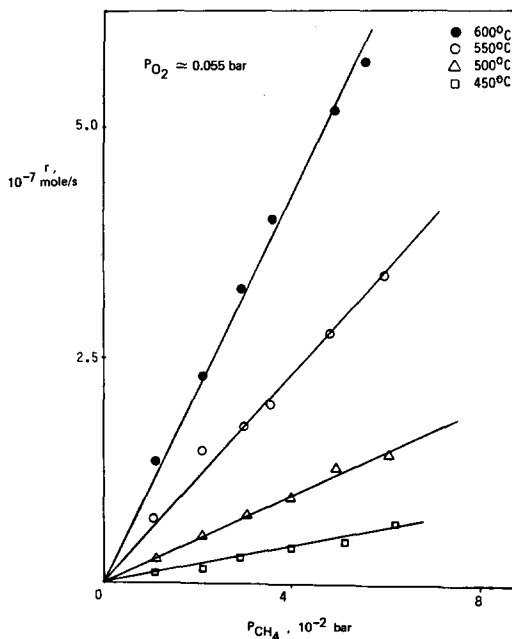


FIG. 3. Dependence of reaction rate on P_{CH_4} .

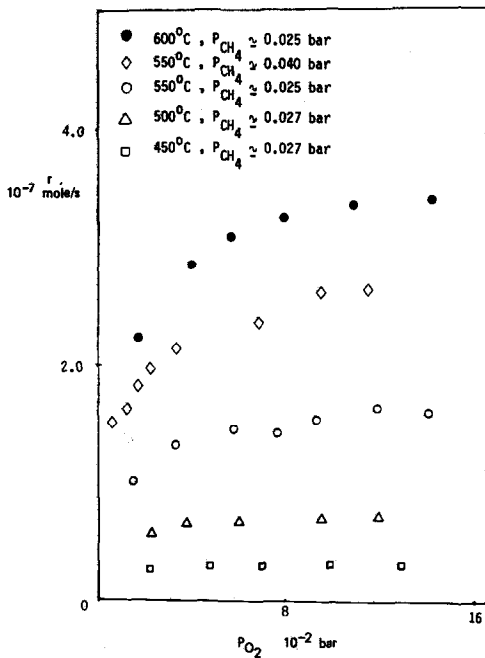


FIG. 4. Dependence of reaction rate on P_{O_2} .

the reactor at constant T and P_{O_2} . Clearly the rate is linearly proportional to methane partial pressure. Figure 4 shows the dependence of the reaction rate on P_{O_2} for constant P_{CH_4} . At low partial pressures of oxygen the rate tends to be proportional to P_{O_2}

while at high P_{O_2} it becomes almost independent of the oxygen partial pressure. It was found that in the range where the rate becomes independent of P_{O_2} all the kinetic data could be expressed rather accurately by

$$r = K_R P_{CH_4} \quad (8)$$

with

$$K_R = 1.97 \exp\left(\frac{-10,300}{T}\right) \text{ mol/s bar.} \quad (9)$$

Oxygen Activity Measurements

It was found that in general, during methane oxidation $a_0 \neq P_{O_2}^{1/2}$, i.e., thermodynamic equilibrium is not established between adsorbed oxygen and oxygen in the gas phase. Nevertheless, the values of a_0 do not differ much from those of $P_{O_2}^{1/2}$, as opposed to the cases of ethylene and propylene oxidation on Ag where $a_0 \ll P_{O_2}^{1/2}$ (18, 21). This is justified by the relatively lower rates obtained during CH_4 oxidation as it is further explained in the Discussion section. The dependence of the surface oxygen activity on the partial pressure of methane for constant P_{O_2} is shown in Fig. 5 for 450 and 600°C. In Fig. 6 a_0 is plotted vs P_{O_2} for con-

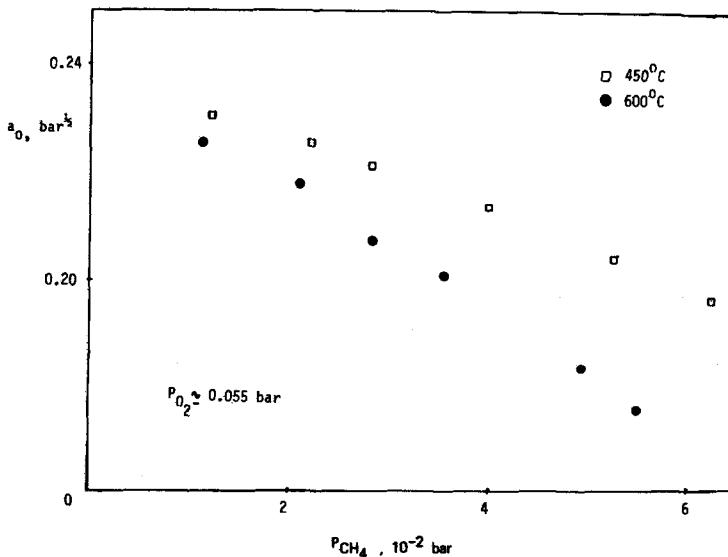


FIG. 5. Dependence of surface oxygen activity a_0 on P_{CH_4} for constant P_{O_2} .

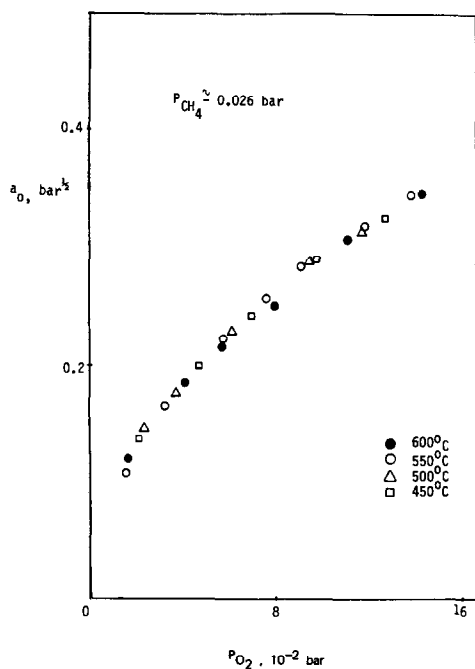


FIG. 6. Dependence of a_0 on P_{O_2} for constant P_{CH_4} .

stant P_{CH_4} for 450–600°C. It can be seen from Figs. 5 and 6 that (a) a_0 increases with increasing P_{O_2} , (b) a_0 decreases weakly with increasing P_{CH_4} , (c) a_0 is almost independent of temperature for constant P_{O_2} and P_{CH_4} .

It was found that all the measurements could be correlated rather accurately by the equation

$$K \left(\frac{P_{O_2}^{1/2}}{a_0} - 1 \right) = K_R P_{CH_4}, \quad (10)$$

where K_R is that given from Eq. (9) and

$$K = 0.172 \exp\left(\frac{-9500}{T}\right) \text{ g atom O/s.} \quad (11)$$

This is shown in Fig. 7. Furthermore the relation between the reaction rate and the surface oxygen activity was found to satisfy the equation

$$P_{CH_4} \cdot r^{-1} = K' a_0^{-1} + K'' \quad (12)$$

with

$$K' = 6.71 \times 10^3 \exp\left(\frac{1800}{T}\right) \frac{\text{s} \cdot \text{bar}^{3/2}}{\text{mol}} \quad (13)$$

and

$$K'' = 0.508 \exp\left(\frac{10,300}{T}\right) \frac{\text{s} \cdot \text{bar}}{\text{mol}}. \quad (14)$$

This is shown in Fig. 8 for 600, 550, and 500°C.

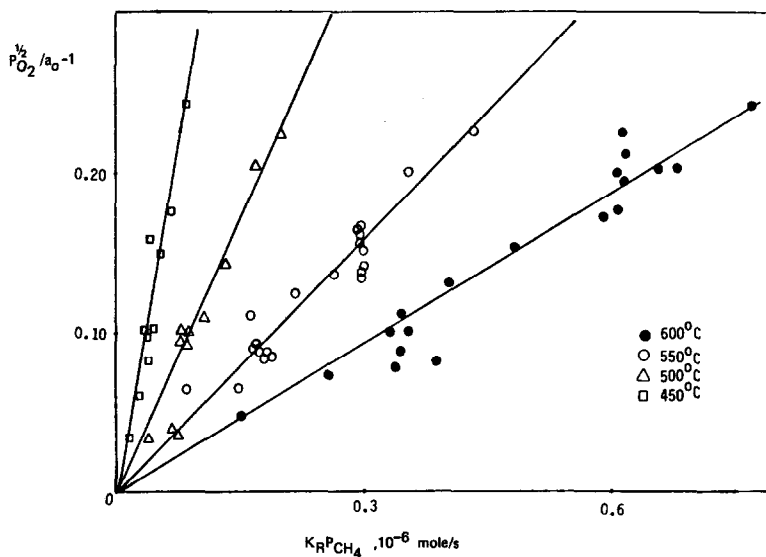
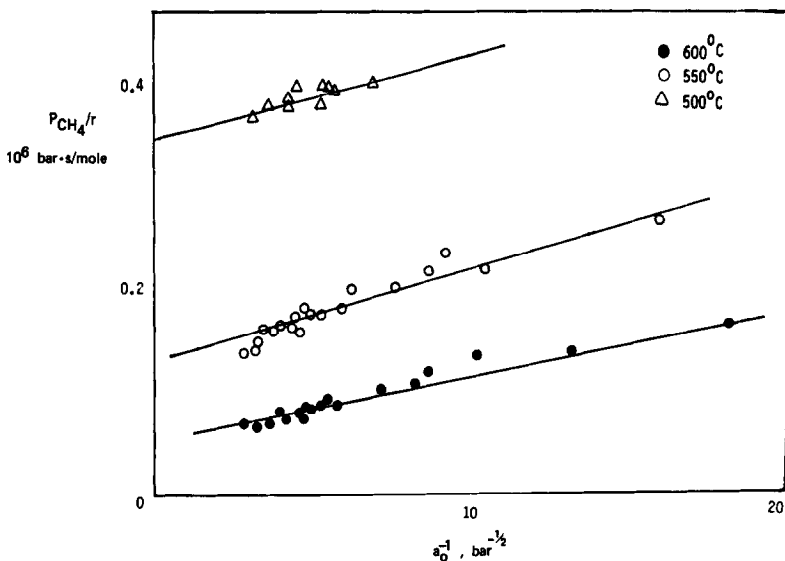


FIG. 7. Dependence of a_0 on gas phase composition.

FIG. 8. Dependence of reaction rate on a_0 .

DISCUSSION

The mechanism of the silver-catalyzed methane oxidation can be now discussed on the basis of the reaction kinetics and the information provided by the solid electrolyte-aided surface oxygen activity measurements. A satisfactory kinetic model should account not only for the kinetics but also for the surface oxygen activity behavior. A reaction model explaining both kinetic and potentiometric observations in a semiquantitative manner is presented below.

Although more than one type of adsorbed oxygen has been reported to exist on silver (18, 29) we will consider only atomic oxygen in this study. This does not imply that atomic oxygen is the only type of oxygen adsorbed on Ag but at the present time we neglect the existence of other types of adsorbed oxygen since we consider the atomic type responsible for the oxidation of methane. In agreement with previous studies on silver we will assume a Langmuir type of adsorption of oxygen on the Ag surface (18, 21). Following the definition of surface oxygen activity a_0 and the Langmuir adsorption assumption one can write

$$\theta_0 = \frac{K_0 a_0}{1 + K_0 a_0}, \quad (15)$$

where θ_0 is the coverage of atomic oxygen on the catalyst surface and K_0 is the adsorption coefficient for atomic oxygen (18, 26). Note that Eq. (15) relates two intrinsic surface properties and is valid whether or not equilibrium with the gas phase exists (20, 26, 27).

Using the information provided by the kinetics and specifically the dependence of the reaction rate on the partial pressure of methane (Fig. 3) an Eley-Rideal type of adsorption-reaction is considered, according to which adsorbed atomic oxygen reacts with gaseous methane. In that case

$$r = K_R P_{\text{CH}_4} \theta_0 \quad (16)$$

Substituting the value of θ_0 from Eq. (15), one obtains

$$r = K_R P_{\text{CH}_4} \frac{K_0 a_0}{1 + K_0 a_0}. \quad (17)$$

Taking the reciprocals of both terms of the above equation and multiplying both by P_{CH_4} it follows that

$$\frac{P_{\text{CH}_4}}{r} = \frac{1}{K_R} + \frac{1}{K_0 K_R} \frac{1}{a_0}, \quad (18)$$

which reduces to the experimentally derived Eq. (12) for $K' = 1/K_0K_R$ and $K'' = 1/K_R$.

The value of K_R is given from Eqs. (8) and (9). Consequently from the values of K' (slopes of the lines in Fig. 8) one can calculate

$$K_0 = 7.56 \times 10^{-5} \exp\left(\frac{8500}{T}\right) \text{ bar}^{-1/2}. \quad (19)$$

Since K_0 is the adsorption coefficient of atomic oxygen on silver it follows from Eq. (19) that $\Delta H_0 = -8,500R = -17 \text{ kcal/g atom O}$ and $\Delta S_0 = -9.5R = -19 \text{ cal/g atom O} \cdot \text{K}$ where ΔH_0 and ΔS_0 are the enthalpy and entropy of adsorption of atomic oxygen.

The surface oxygen activity dependence on temperature and gas composition can be explained by considering a steady state mass balance for adsorbed atomic oxygen:

$$K_A P_{O_2}^{1/2} (1 - \theta_0) = K_D \theta_0 + K_R P_{CH_4} \theta_0. \quad (20)$$

The left-hand side term corresponds to atomic oxygen adsorption. Experimental justification for first-order adsorption and desorption terms has been provided previously (26). The right-hand side terms correspond to desorption and reaction with gaseous methane. Dividing Eq. (20) by $K_A (1 - \theta_0)$ one obtains

$$P_{O_2}^{1/2} = \frac{K_D}{K_A} \frac{\theta_0}{1 - \theta_0} + \frac{K_R}{K_A} \frac{\theta_0}{1 - \theta_0} \cdot P_{CH_4}. \quad (21)$$

Taking into account Eq. (15) and that $K_0 = K_A/K_D$, Eq. (21) becomes

$$P_{O_2}^{1/2} = a_0 \left(1 + \frac{K_R}{K_D} P_{CH_4}\right)$$

or

$$\frac{P_{O_2}^{1/2}}{a_0} - 1 = \frac{K_R}{K_D} P_{CH_4}, \quad (22)$$

which reduces to the experimental observation (10) for $K = K_D$. Thus K is interpreted as the desorption coefficient for atomic oxygen and following Eq. (11) we can write

$$K_D = 0.172 \exp\left(\frac{-9500}{T}\right) \text{ g atoms O/s}. \quad (23)$$

The value of K_D is in good agreement with previous studies of ethylene and propylene oxidation over silver catalysts (21).

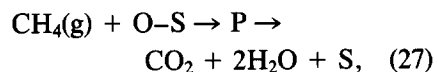
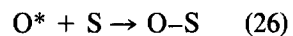
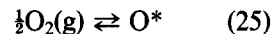
The right-hand side term of Eq. (22) is proportional to the reaction rate (Eq. (8)). Hence for low values of the rate of CH_4 oxidation the quantity $P_{O_2}^{1/2}/a_0 - 1$ also becomes very small or $P_{O_2}^{1/2} \rightarrow 1$ or $P_{O_2}^{1/2} \approx a_0$, which implies very small or negligible deviation from equilibrium between adsorbed and gaseous oxygen.

From the values of K_0 and K_D given from Eqs. (19) and (23), respectively, we can further calculate the adsorption rate constant K_A for atomic oxygen

$$K_A = K_0 K_D = 1.3 \times 10^{-5} \exp\left(\frac{-1000}{T}\right) \frac{\text{g atom O}}{\text{s} \cdot \text{bar}^{1/2}} \quad (24)$$

which shows that the adsorption of atomic oxygen is slightly activated (about 2 kcal/g atom O).

The above kinetic model explains both kinetic and potentiometric results in a satisfactory manner. The reaction rate expression given in Eq. (16) implies that one oxygen atom is involved in the rate-limiting step. Hence the following reaction scheme could satisfy the experimental results



where P stands for a reactive intermediate which is rapidly oxidized to CO_2 and H_2O , O^* stands for oxygen in a precursor adsorption state (26), and S stands for a surface site on the Ag catalyst.

In summary the present work showed that methane and oxygen react on Ag catalysts to produce mainly CO_2 and H_2O . The kinetics are in agreement with an Eley-

Rideal type of adsorption-reaction. Additional information about the role of the silver surface could be extracted by using surface techniques other than SEP, such as infrared spectroscopy. It will be very interesting to examine the product distribution in presence of halogen promoters. Furthermore since oxygenated products have been seen to increase in yield when using a zirconia cell as an oxygen pump, the effect of oxygen "pumping" during methane oxidation deserves investigation. Work toward that goal is already in progress.

ACKNOWLEDGMENTS

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REFERENCES

- Margolis, L. Y., "Advances in Catalysis," Vol. 14, p. 429. Academic Press, New York, 1963.
- Dixon, J. K., and Longfield, J. E., in "Catalysis" (P. H. Emmett, Ed.), Vol. 7. Reinhold, New York, 1960.
- Walker, J. F., "Formaldehyde," 3rd ed. Reinhold, New York, 1967.
- Kirk-Othmer, "Encyclopedia of Chemical Technology," 3rd ed. New York, Wiley, 1978.
- Satterfield, C. N., "Heterogeneous Catalysis in Practice." McGraw-Hill, New York, 1980.
- Cullis, C. F., Keene, D. E., and Trimm, D. L., *J. Catal.* **19**, 378 (1970).
- Firth, J. G., *Trans. Faraday Soc.* **62**, 2566 (1966).
- Firth, J. G., and Holland, H. B., *Nature (London)* **217**, 1252 (1968).
- Reyerson, L. H., and Swearingen, L. E., *J. Phys. Chem.* **31**, 88 (1927).
- Mann, R. S., and Dosi, M. K., *J. Chem. Technol. Biotechnol.* **29**, 467 (1979).
- Schonfelder, R., *Ber. Ges. Kohlentech.* **247** (1923).
- Berl, K., and Fischer, B., *Z. Angew. Chem.* **36**, 297 (1923).
- Anderson, R. B., Stein, K. C., Feenan, J. J., and Hofer, L. J. E., *Ind. Eng. Chem.* **53**, No. 10, 809 (1961).
- Yung-Fang Yu Yao, *Ind. Eng. Chem. Proc. Res. Dev.* **19**, 293 (1980).
- Stoukides, M., and Vayenas, C. G., *ACS Symp. Ser.* **178**, 181 (1982).
- Stoukides, M., and Vayenas, C. G., *J. Catal.* **70**, 137 (1981).
- Seimanides, S., and Stoukides, M., in preparation.
- Stoukides, M., and Vayenas, C. G., *J. Catal.* **69**, 18 (1981).
- Vayenas, C. G., and Saltsburg, H., *J. Catal.* **57**, 236 (1979).
- Vayenas, C. G., Lee, B., and Michaels, J., *J. Catal.* **66**, 36 (1980).
- Stoukides, M., and Vayenas, C. G., *J. Catal.* **82**, 45 (1983).
- Pancharatnam, S., Huggins, R. A., and Mason, D., *J. Electrochem. Soc.* **122**, 869 (1975).
- Gür, T. M., and Huggins, R. A., *Solid State Ionics* **5**, 567 (1981).
- Etsell, T. H., and Flengas, S. N., *J. Electrochem. Soc.* **118**(12), 1980 (1971).
- Vayenas, C. G., and Farr, R. D., *Science* **208**, 593 (1980).
- Stoukides, M., and Vayenas, C. G., *J. Catal.* **64**, 18 (1980).
- Wagner, C., "Advances in Catalysis," Vol. 21, p. 323. Academic Press, New York, 1970.
- Seimanides, S. M.S. thesis, Tufts University, 1984.
- Kilty, R. A., and Sachtler, W. M. H., *Catal. Rev.-Sci. Eng.* **10**(1), 1 (1974).