

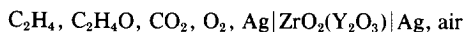
The Effect of Electrochemical Oxygen Pumping on the Rate and Selectivity of Ethylene Oxidation on Polycrystalline Silver

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The selectivity and ethylene oxide yield of ethylene oxidation on polycrystalline silver can be affected significantly by electrochemical oxygen pumping. The reaction was studied in the solid electrolyte cell



at temperatures near 400°C and atmospheric pressure. Under open-circuit conditions the porous silver electrode exposed to the ethylene-O₂ mixture acts as a normal catalyst for C₂H₄ oxidation to C₂H₄O and CO₂. It was found that when external voltages are applied to the cell and O²⁻ is "pumped" to the catalyst, the ethylene oxide selectivity and yield increase considerably. The opposite effect is observed upon inversion of the voltage polarity. The increase in the rate of C₂H₄O production can exceed the rate of O²⁻ pumping by a factor of 400, indicating a dramatic change in the properties of the silver catalyst. The phenomenon is reversible and typical relaxation times are of the order of a few minutes. A simple model is proposed in order to explain this new phenomenon.

INTRODUCTION

The silver-catalyzed ethylene epoxidation has been studied extensively over the last 30 years. Work in this area prior to 1974 has been reviewed by Kilty and Sachtler (1). More recently Force and Bell have studied the infrared spectra of species adsorbed on silver during ethylene oxidation (2) and examined the relationship of these species to the reaction mechanism (3). Harriot *et al.* (4) have studied the effects of catalyst support and crystal size on activity and selectivity. Cant and Hall (5) used ¹⁴C to study oxygen exchange between ethylene and ethylene oxide and found that ethylene oxide oxidation to CO₂ is much slower than direct CO₂ formation from ethylene oxidation, in agreement with previous kinetic studies (1, 6). Recent UHV studies have shown conclusively that CO₂ is the only product of ethylene reaction

with atomic oxygen (7), in agreement with previous studies on the interaction of N₂O and ethylene on silver (8). Kinetic measurements in a well-mixed reactor have been recently combined with simultaneous *in situ* measurement of the thermodynamic activity of oxygen on porous silver catalyst films (9, 10).

A number of different approaches have been examined so far in order to increase the intrinsic selectivity of silver to ethylene oxide. These include alloying silver with other metals (11), using different catalyst support and promoters (4, 12), as well as adding gas phase chlorinated hydrocarbon moderators which definitely improve the selectivity and are used in industry (12). Carberry *et al.* have also found that the selectivity increases with γ -irradiation of the catalyst (13).

In the present communication we describe a new technique for altering the intrinsic activity and selectivity of silver for ethylene oxidation. A porous silver catalyst film exposed to ethylene and O₂ is used as

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one electrode of a solid electrolyte cell. When an external voltage is applied to the cell, O^{2-} is pumped electrochemically to the catalyst. The activity of oxygen species adsorbed on silver can thus be dramatically altered. This can cause a significant change in catalyst activity and selectivity.

Zirconia cells similar to the ones employed in the present study, have been used

(i) by Mason *et al.* to electrochemically remove oxygen from Pt and Au and significantly enhance the rate of NO decomposition (14, 15);

(ii) by Farr and Vayenas to electrochemically oxidize ammonia and co-generate NO and electric energy (16, 17);

(iii) by Vayenas and co-workers (9, 10, 18, 19) to study the mechanism of several metal-catalyzed oxidations under open circuit (potentiometric) conditions.

The anodic oxidation of ethylene in a low-temperature aqueous electrolyte electrochemical cell has been studied by Holbrook and Wise (20). It was found that product selectivity (carbonate vs ethylene glycol) depends on the potential of the silver anode.

EXPERIMENTAL METHODS

The experimental apparatus has been described in detail elsewhere (9, 10, 18). A schematic diagram of the reactor cell is shown in Fig. 1. In a previous communication (9) we have also described the porous silver catalyst film deposition and characterization procedure. Auger Electron Spectroscopy was used to examine the Ag surface, which was found to be fairly clean (9).

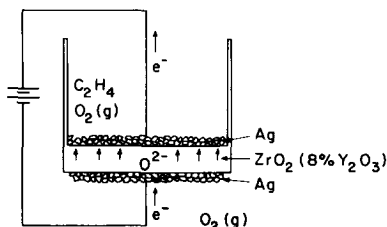


FIG. 1. Schematic diagram of the solid electrolyte cell reactor.

The various porous silver films employed in the present study had a superficial surface area of 2 cm^2 and true surface areas varying between 100 and 1500 cm^2 , corresponding to reactive oxygen uptakes Q of order 10^{-7} to 10^{-6} moles O_2 . These surface areas roughly correspond to 1 m^2 of surface area per gram of Ag catalyst. Once the surface area of a Ag porous film had been estimated using ethylene/ O_2 titration (9), the surface areas of other films was determined by comparing their steady-state catalytic activity with that of the original film at a set of standard conditions ($P_{ET} = 10^{-2}$ bar, $P_{O_2} = 5 \times 10^{-2}$ bar, $T = 400^\circ\text{C}$). Thus there can be only a systematic error in the surface area measurement of different films.

Reactants were certified standards of ethylene diluted in N_2 and Matheson zero-grade air. They could be further diluted in N_2 . No chlorinated hydrocarbon moderators were employed in the present study. Reactants and products were analyzed by on-line gas chromatography. The concentration of byproduct CO_2 in the reactor effluent stream was also continuously monitored by means of a nondispersive ir CO_2 Analyzer (Beckman 864).

The flat bottom of the zirconia solid electrolyte tubes were diamond polished to thicknesses of the order of $200 \mu\text{m}$ in order to reduce the resistance of the cell. Constant voltages or currents were applied to the cell using an AMEL 549 potentiostat-galvanostat. Most runs were done galvanostatically, i.e., by maintaining the imposed current constant. The voltage drop across the cell was continuously monitored with a J. Fluke 891 A differential voltmeter and the current through the cell could also be measured by a J. Fluke 8040 A multimeter.

RESULTS

Close agreement was observed ($\pm 1\%$) between measured and theoretical emf values when O_2 , N_2 , or He mixtures of known P_{O_2} were fed through the zirconia cell reactor. This verified the pure ionic

conductivity of the solid electrolyte. When ethylene-oxygen mixtures are fed through the reactor, the open circuit emf E , which reflects the oxygen activity a_0^2 on the catalyst (9, 10) according to

$$E = RT/4F \ln a_0^2/(0.21), \quad (1)$$

takes values between -10 and -80 mV indicating that $a_0^2 < P_{O_2}$, because the intrinsic rate of oxygen adsorption is comparable to the rate of the surface oxidation steps (9, 10).

The Effect of Electrochemical Oxygen Pumping

Several different zirconia reactor cells were used in the course of the experiments. The cells differed in zirconia thickness and in the surface area S of the silver catalyst electrode. Figure 2 shows the effect of applying a constant current $i = \pm 800 \mu A$ to cell reactor 1, while monitoring the rate of ethylene epoxidation, r_1 , and the rate of ethylene oxidation to CO_2 , r_2 , at a residence time of 6.5 s. At the start of the experiment the circuit is open and the catalyst is at steady-state activity and selectivity. The reactive oxygen uptake Q of the silver catalyst electrode of cell reactor 1 is 1.4×10^{-7} moles O_2 . At time $t = 0$ the

galvanostat is used to apply a current $i = -800 \mu A$ with a corresponding rate of oxygen removal from the catalyst $G_{O_2} = i/4F = 2 \times 10^{-9}$ moles O_2/s . This causes a decrease in r_1 and r_2 . The decrease in the total rate of oxygen consumption, i.e., $0.5\Delta r_1 + 3\Delta r_2$, is approximately 7 times greater than G_{O_2} . The decrease in r_1 is larger than the corresponding decrease in r_2 , thus selectivity drops. At the same time the voltage V of the cell gradually changes from $V = E = -65$ mV to a steady-state value $V \approx -2$ V, with a relaxation time constant approximately equal to that of r_1 and r_2 . Subsequently the circuit is opened and r_1, r_2 , and V are restored to their intrinsic values within 3–4 min. The galvanostat polarity is then reversed and a current $i = 800 \mu A$ is applied to the cell with a corresponding rate of oxygen transport to the catalyst $G_{O_2} \approx 2 \times 10^{-9}$ mole/s. This causes an increase in r_1 and r_2 , which is considerably larger than G_{O_2} . Since the increase in r_1 is greater, selectivity increases. At the same time the cell voltage gradually reaches a steady-state value $V \approx 2$ Volts. Finally the circuit is opened again and the catalyst activity and selectivity as well as the open-circuit emf relax to their initial values within a few minutes. Thus the phenomenon is reversible and no permanent change of the silver catalyst has taken place.

During the course of the experiments it was found that voltages in excess of approximately ± 2.5 V should not be applied to the cell because this causes electrolysis of the solid electrolyte at these relatively low temperatures. Once zirconia has been reduced to metallic zirconium the cell resistance drops precipitously, the open-circuit emf drops to zero, no oxygen can be pumped to the catalyst, and the phenomenon disappears.

In Fig. 3 the effect of oxygen pumping to the catalyst is shown at lower current densities. Figures 3 through 7 refer to the catalyst of reactor cell 2 (Table 1). Before $t = 0$ the circuit is open and the catalyst is at steady state with a constant rate of ethylene

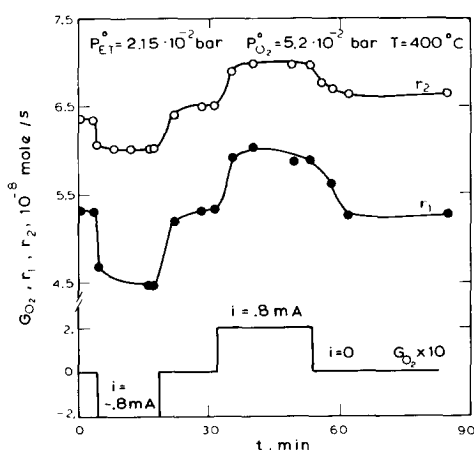


FIG. 2. Effect of electrochemical oxygen pumping on the rate of ethylene epoxidation r_1 and deep oxidation r_2 . Comparison with the rate of oxygen transport through the electrolyte $G_{O_2} = i/4F$.

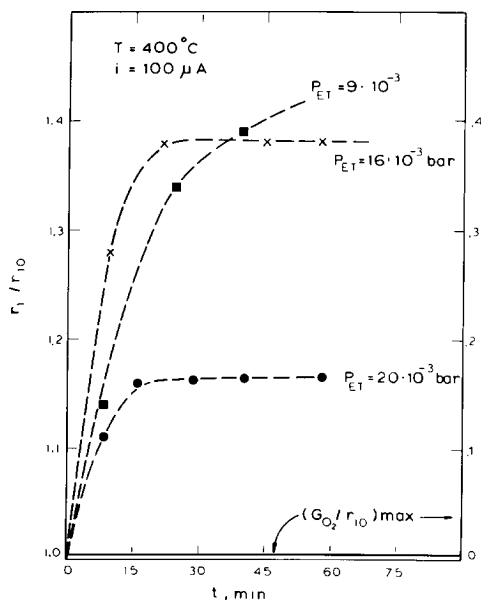


FIG. 3. Transient behavior of the rate of ethylene epoxidation r_1 when a constant current $i = 100 \mu\text{A}$ is applied at $t = 0$. The P_{O_2} values were 13.5×10^{-2} , 10×10^{-2} and 6×10^{-2} bar for P_{ET} equal to 9×10^{-3} , 16×10^{-3} , and 20×10^{-3} bar, respectively.

epoxidation r_{10} ($\approx 5.0 \times 10^{-6} \cdot P_{\text{ET}}$ moles/s). At $t = 0$, a constant current $i = 100 \mu\text{A}$ is applied to the cell and oxygen is pumped to the catalyst at a constant rate $G_{\text{O}_2} \approx 2.6 \times 10^{-10}$ moles/s. The rate of epoxidation r_1 increases considerably. The bottom horizontal line $(G_{\text{O}_2}/r_{10})_{\text{max}} \approx 2.5 \times 10^{-3}$ corresponds to $P_{\text{ET}} \approx 2 \times 10^{-2}$ ($r_{10} = 1.02 \times 10^{-7}$ mole/s) and shows the anticipated maximum relative increase in r_1 on the basis of

TABLE I

Effect of Electrode Surface Area on the Experimental Relaxation Time Constant τ_c and Comparison with $4FQ/i$

Catalyst	$Q = \text{Oxygen uptake}$ (moles $\text{O}_2 \times 10^{-7}$)	τ_c (min)	$4FQ/i$ (min)
3	0.45	13.5	5.8
2	2.3	22.5	29.6
4	2.5	25.	32.2
5	20.	> 100	257.

^a $i = +50 \mu\text{A}$, $P_{\text{ET}} = 1.6 \times 10^{-2}$ bar, $P_{\text{O}_2} = 6 \times 10^{-2}$ bar.

the rate of oxygen transport to the catalyst through the electrolyte. Stated differently, if the nature of the catalyst were not changing during oxygen pumping and each O^{2-} ion pumped to the catalyst produced one ethylene oxide molecule, then the increase in r_1 would be smaller or equal ($P_{\text{ET}} \approx 2 \times 10^{-2}$ bar) to $(G_{\text{O}_2}/r_{10})_{\text{max}}$. Thus the increase in r_1 is here 160 and 360 times greater than the increase corresponding to the rate of electrochemical oxygen pumping, for $P_{\text{ET}} = 2 \times 10^{-2}$ and 9×10^{-3} bar, respectively.

The corresponding transient effect on the rate of CO_2 production r_2 is shown in Fig. 4. The increase in r_2 is two orders of magnitude larger than G_{O_2} but smaller than the increase in r_1 , thus selectivity to ethylene oxide increases. An interesting feature of Figs. 3 and 4 is the decrease in the relaxation time constant of the system with increasing P_{ET} . The relaxation time τ_c is defined as the time required to reach 63% of the final steady-state rate increase.

The effect of varying the imposed current at constant gas phase composition is shown in Figs. 5 and 6. At times before $t = 0$ the

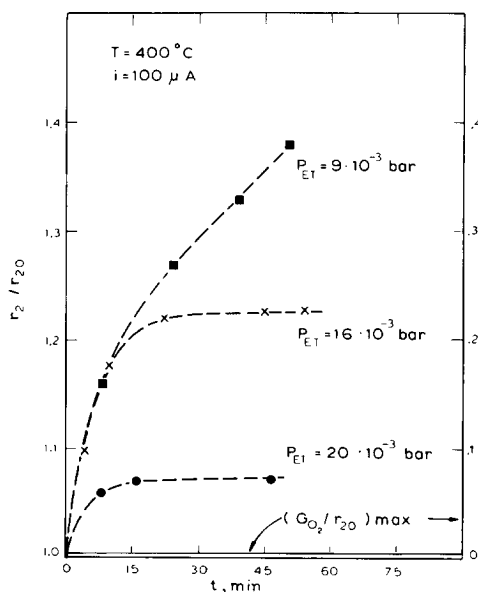


FIG. 4. Transient behavior of the rate of ethylene deep oxidation r_2 when a constant current $i = 100 \mu\text{A}$ is applied at $t = 0$. Oxygen partial pressures as in Fig. 3.

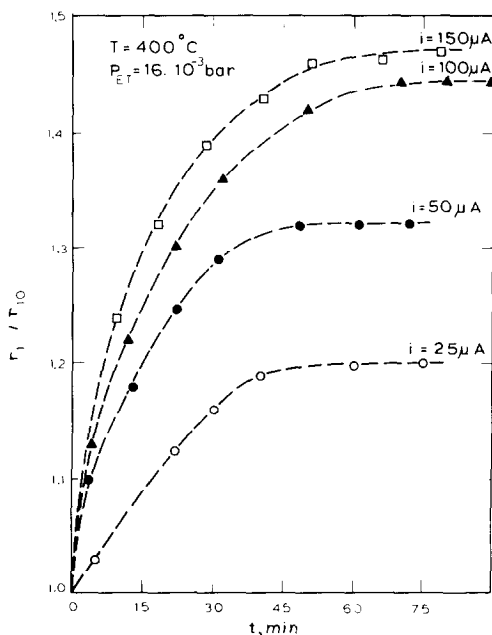


Fig. 5. Transient effect on r_1 when different currents are applied at $t = 0$. ($P_{O_2} = 0.1 \text{ bar}$.)

circuit is open and the catalyst is at steady state with a constant rate of ethylene epoxidation $r_{10} = 0.89 \times 10^{-7} \text{ moles/s}$. At time $t = 0$, a constant current is applied and the transient increase in r_1 and r_2 is monitored. It can be seen that the relaxation time constant of the system decreases slightly with increasing current. It is also clear that

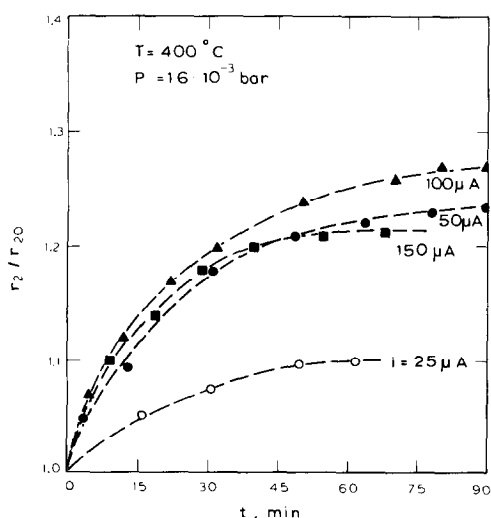


Fig. 6. Transient effect on r_2 when different currents are applied at $t = 0$. ($P_{O_2} = 0.1 \text{ bar}$.)

increasing the imposed current in excess of $100 \mu\text{A}$ does not produce any additional increase in r_1 and r_2 . This is shown in Fig. 7, where the steady-state increases Δr_1 and Δr_2 in the rates of ethylene epoxidation and combustion are plotted vs imposed current. Since the increase in r_1 is considerably higher than that in r_2 , the selectivity increases. The bottom line in Fig. 7 corresponds to the ratio of the rate of oxygen pumping to the catalyst over the intrinsic rate of oxygen consumption, taking into account that the intrinsic selectivity is of order 0.5. If the specific rate on the catalyst were not changing due to oxygen pumping then $\Delta r_1 / r_{10}$ and $\Delta r_2 / r_{20}$ would collapse into the bottom line $G_{O_2} / (r_{10} / 2 + 3r_{20})$. Because Δr_1 and Δr_2 do not increase with current for $i > 100 \mu\text{A}$, it becomes clear why Δr_1 and Δr_2 are only 7 times larger than G_{O_2} for $i = 800 \mu\text{A}$ (Fig. 2).

Figures 8 and 9 show the transient effect of oxygen pumping on the selectivity and ethylene oxide yield of reactor cell 3. Here the intrinsic selectivity and yield (moles ethylene oxide produced per mole of ethylene fed to the reactor) are 0.52 and 2.2×10^{-2} respectively at $P_{ET} = 1.5 \times 10^{-2} \text{ bar}$ and $P_{O_2} = 0.1 \text{ bar}$.

The magnitude of Δr_1 and Δr_2 was found to increase with increasing P_{O_2} / P_{ET} ratio and to be only weakly dependent on the electrode surface area. Since the intrinsic rates r_{10} and r_{20} are proportional to the electrode surface area the relative rate changes $\Delta r_1 / r_{10}$, $\Delta r_2 / r_{20}$ as well as the change in selectivity become more pronounced when the catalyst electrode has small surface area, e.g., reactor cell 3 (Table 1 and Figs. 8 and 9). A quantitative account of the role of the gas phase composition, temperature electrode surface area, and cell overvoltage on the transient and steady-state behavior of these cells will be given in a later communication (21).

Oxygen pumping to the catalyst (Fig. 8) causes the selectivity to increase to 0.59 while the yield almost doubles. Oxygen pumping from the catalyst (Fig. 9) reduces

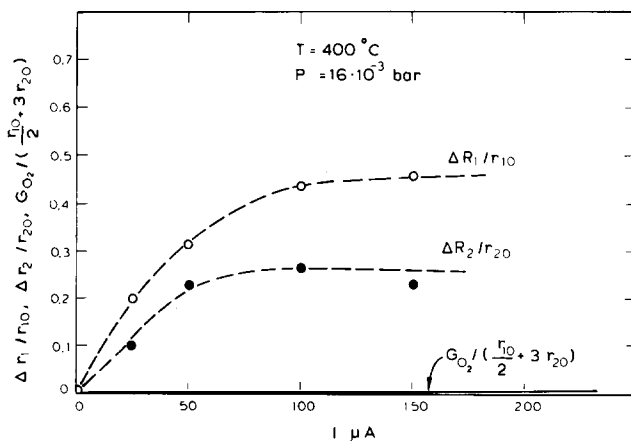


FIG. 7. Effect of current on the steady-state increase in the rate of ethylene epoxidation and combustion. Comparison with rate of oxygen pumping to the catalyst. Intrinsic ($i = 0$) selectivity ~ 0.5 . ($P_{\text{O}_2} = 0.1 \text{ bar}$.)

the selectivity to 0.42 and the yield to 1.1×10^{-2} . Thus the selectivity changes from 0.42 to 0.59 and the yield from 1.1×10^{-2} to 4.4×10^{-2} by simply applying a current of $\pm 50 \mu\text{A}$ to the cell.

DISCUSSION

The observed phenomena clearly show that the nature of the silver catalyst is changing significantly during electrochemical oxygen pumping. The increase in the rate of ethylene epoxidation and deep oxidation is more than two orders of magnitude

greater than the rate of oxygen pumping through the electrolyte. The selectivity also changes considerably. It can be easily shown that the electrolyte temperature cannot rise locally more than 2 K at most, due to I^2R heat generated during oxygen pumping. This was also shown by measuring the temperature of the electrolyte at a distance of 1 mm from the two electrodes and observing no measurable temperature rise during pumping. The absence of local catalyst heating due to oxygen pumping is also demonstrated by the fact that upon revers-

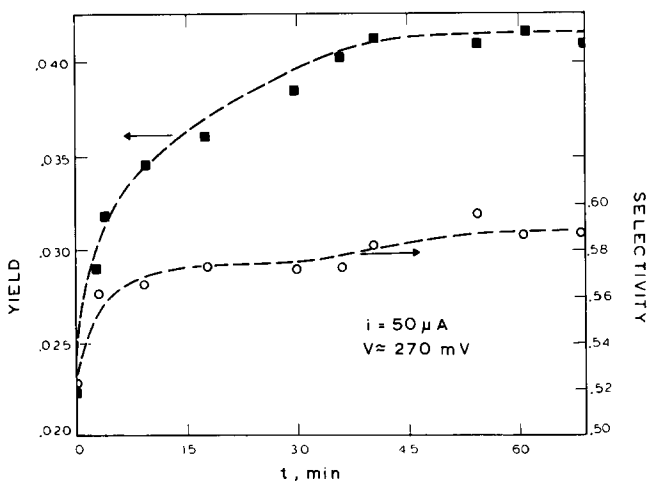


FIG. 8. Transient effect of oxygen pumping to the catalyst on selectivity and yield of ethylene oxide (reactor 3). Current applied at $t = 0$. Temperature: 400°C .

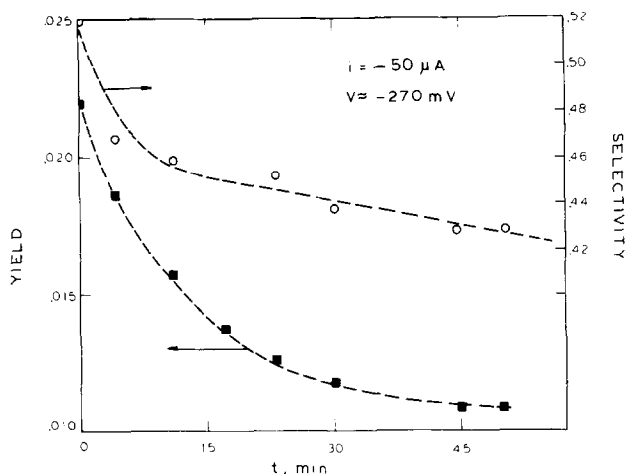


FIG. 9. Transient effect of electrochemical oxygen removal from the catalyst on selectivity and yield of ethylene oxide (reactor 3). Current applied at $t = 0$. Temperature: 40°C .

ing the direction of pumping both r_1 and r_2 decrease (Fig. 2).

Internal gas phase diffusional limitation inside the porous silver film are totally absent under the conditions of these experiments (9, 10). External concentration gradients have also been shown to be negligible (9, 10). Thus it can be safely concluded that it is the intrinsic properties of the silver catalyst that change during electrochemical oxygen pumping.

When oxygen is pumped to the catalyst the thermodynamic activity of oxygen on the silver catalyst electrode increases considerably because of the external voltage applied. It thus becomes possible to at least partly oxidize the silver catalyst electrode. The experimentally observed relaxation time constants of the system show conclusively that this process must involve surface rather than bulk oxidation of the silver crystallites. The polycrystalline Ag films used could adsorb typically $Q = 2 \times 10^{-7}$ moles O_2 . Typical currents employed in the present study were of order $100 \mu\text{A}$ corresponding to 2.6×10^{-10} moles O_2/s transported through the electrolyte. Thus the time required to fully cover the silver surface with surface oxide is of order 12 min in good agreement with the experimental relaxation time (Table 1).

If, on the other hand, oxygen pumping

caused bulk oxidation of the silver catalyst this would require approximately 2×10^{-4} moles O_2 . With currents of order $100 \mu\text{A}$ this would correspond to time constants of about 50 h. It therefore follows that the observed phenomenon is due to surface oxidation of the silver crystallites. The phenomenon may be related to that observed during anodic oxidation of ethylene on a silver electrode in a low-temperature aqueous solution electrochemical cell (20) despite the significant differences in temperature and electrolyte material.

One can only speculate about the nature of the surface silver oxide formed during oxygen pumping to the catalyst and about its relation to the various forms of chemisorbed oxygen found on silver (1). Infrared spectroscopic studies of the catalyst during pumping should prove useful for elucidating the nature of the surface specie which is responsible for the observed phenomenon. It seems however that this chemisorbed oxygen species or surface oxide preexists on silver before pumping. Otherwise it is difficult to explain the dramatic decrease in r_1 and r_2 upon pumping oxygen away from the catalyst (Figs. 2 and 9).

"Macroscopic" Transient and Steady-State Model

Although the exact nature of the surface

silver-oxygen species or surface oxide formed and destroyed during electrochemical O_2^- pumping to and from the silver catalyst respectively is not known, it was found that a simple kinetic model could explain almost all the macroscopic features of the oxygen pumping effect in a semi-quantitative manner. This model represents a first attempt to understand the new phenomenon and could be refined and/or modified as more information becomes available about the silver-oxygen species created and destroyed during oxygen pumping. However, the model even in the present form can explain

(a) The increase in steady state Δr_1 and Δr_2 with increasing current i followed by roughly constant Δr_1 and Δr_2 for i greater than $50 \mu A/cm^2$ (Fig. 7).

(b) The decrease in $\Delta r_1/r_{10}$ and $\Delta r_2/r_{20}$ with increasing P_{ET}/P_{O_2} at constant i (Figs. 3 and 4).

(c) The observed decrease in the relaxation time constant τ_c with increasing current at constant P_{ET} (Figs. 5 and 6).

(d) The observed decrease in τ_c with increasing P_{ET}/P_{O_2} at constant current (Figs. 3 and 4).

(e) The observation that τ_c increases with increasing surface area of the silver catalyst electrode (Table 1).

The model is based on the hypothesis that oxygen pumping to the catalyst causes an increase in the surface concentration of active silver oxide. The activity and selectivity on the surface of this silver oxide, denoted by AgO_2^* , is assumed higher than that on reduced silver. In order to account for the experimentally observed increase in the relaxation time constant with increasing P_{O_2}/P_{ET} ratio it becomes necessary to postulate that AgO_2^* forms on sites adjacent to chemisorbed oxygen. We first consider a mass balance for O_2^* :

$$S \cdot \theta_{O_2} \cdot \frac{dc}{dt} = \frac{i}{4F} \left(1 - \frac{c}{c_M} \right) + K_1 \cdot S \cdot \theta_{O_2} (c_M - c) - K_2 \cdot S \cdot P_{ET} \cdot c, \quad (2)$$

where $S(cm^2)$ is the surface area of the silver catalyst electrode, θ_{O_2} is the surface coverage of molecularly adsorbed oxygen on the reduced silver surface, c (moles O_2/cm^2) is the surface concentration of AgO_2^* , c_M is the saturation surface concentration of AgO_2^* corresponding to full coverage of sites available for oxide formation, and $K_1 (s^{-1}cm^{-2})$ and $K_2 (bar^{-1} \cdot s^{-1} \cdot cm^{-2})$ are specific rate constants for O_2^* formation and destruction from molecularly adsorbed oxygen and gaseous ethylene, respectively. The first term on the right side of Eq. (2) corresponds to O_2^* formation due to electrochemical oxygen pumping. We assumed that no multiple layers of surface oxide can form.

It follows from (2) that the steady-state concentration c of AgO_2^* is

$$\frac{c}{c_M} = \frac{(i/4FSc_M) + K_1\theta_{O_2}}{(i/4FSc_M) + K_1\theta_{O_2} + K_2 \cdot P_{ET}}. \quad (3)$$

According to (3), if no current is applied to the cell the oxide coverage c_0 is given by

$$c_0/c_M = K_1\theta_{O_2}/(K_1\theta_{O_2} + K_2P_{ET}). \quad (4)$$

Therefore the steady-state increase $\Delta c = c - c_0$ in the concentration of AgO_2^* is

$$\Delta c/c_M = (i/4FSc_M) \cdot K_2P_{ET} / \{[(i/4FSc_M) + K_1\theta_{O_2} + K_2P_{ET}] [K_1\theta_{O_2} + K_2P_{ET}]\}. \quad (5)$$

At temperatures above $350^\circ C$ the rates of ethylene epoxidation and combustion on polycrystalline silver have been found to be first order in ethylene and near zero order in oxygen [10]

$$r_{j0} = k_{j0} \cdot S \cdot P_{ET}. \quad (6)$$

In view of Eq. (5) and in order to account for the observed increase in Δr_j with increasing P_{O_2}/P_{ET} ratio one must assume that the rates of epoxidation ($j = 1$) and combustion ($j = 2$) on the silver oxide AgO_2^* are first order in gaseous oxygen

$$\Delta r_j = k_j \cdot S \cdot P_{O_2} \cdot \Delta c, \quad (7)$$

where $k_j (s^{-1} bar^{-1})$ are rate constants for

ethylene epoxidation ($j = 1$) and combustion ($j = 2$) on the oxide. Combining with Eq. (5) one obtains

$$\Delta r_j = \frac{(i/4F) \cdot k_j \cdot K_2 \cdot P_{O_2} \cdot P_{ET}}{\{[(i/4F)S c_M] + K_1 \theta_{O_2} + K_2 P_{ET}\} [K_1 \theta_{O_2} + K_2 P_{ET}]} \quad (8)$$

and according to (6) one obtains

$$\Delta r_j / r_{j0} = \frac{k_j \cdot K_2 \cdot (i/4F) \cdot P_{O_2}}{k_{j0} \cdot S} \frac{1}{\{[(i/4F)S c_M] + K_1 \theta_{O_2} + K_2 P_{ET}\} [K_1 \theta_{O_2} + K_2 P_{ET}]} \quad (9)$$

With $\theta_{O_2} \approx 1$ the steady-state equation (9) explains both steady-state observations (a) and (b). It also explains two additional observations; i.e., that Δr_j vanishes when $P_{O_2} = 0$ and that the relative rate increases $\delta r_j / r_{j0}$ is large for reactors with small electrode surface area S .

Furthermore one can solve Eq. (2) which describes the transient behavior of the system to obtain

$$\begin{aligned} [c - c(0)] / c_M &= \left[\frac{(i/4F)S c_M + K_1 \theta_{O_2}}{(i/4F)S c_M + K_1 \theta_{O_2} + K_2 P_{ET}} \right. \\ &\quad \left. - \frac{c(0)}{c_M} \right] (1 - e^{-t/\tau_c}), \quad (10) \end{aligned}$$

with

$$\tau_c = \frac{S c_M \theta_{O_2}}{(i/4F) + K_1 S c_M \theta_{O_2} + K_2 S c_M P_{ET}} \quad (11)$$

It can be seen that Eq. (11) explains well the three transient experimental observations (c), (d), and (e), i.e., the increase in the relaxation time constant of the system with decreasing current and P_{ET} and increasing electrode surface area.

CONCLUSIONS

The intrinsic rate and selectivity of ethylene oxidation on polycrystalline silver supported on stabilized zirconia can be altered significantly by means of electrochemical O^{2-} pumping to or from the silver catalyst. The yield and selectivity to ethylene oxide increase when O^{2-} is pumped to the cata-

lyst. The relaxation time constant of the system is of order $S c_M F / i$. The increase in the rate of ethylene oxide and CO_2 production can exceed the rate of oxygen pumping by two orders of magnitude.

This phenomenon is clearly of potential practical importance for the manufacture of ethylene oxide. A systematic study of the effects of various design and operating parameters such as silver film purity and porosity, electrolyte thickness, temperature, and feedstream composition is currently underway in order to establish optimal conditions for maximum selectivity to ethylene oxide.

We note that this is the first known application of electrochemical oxygen pumping through a solid electrolyte to alter the selectivity of a heterogeneous catalytic reaction. The application of external voltages to solid electrolytes with appropriate catalytic electrodes may be a powerful technique for influencing the selectivity of other partial catalytic oxidations as well.

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