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The Effects of Dislocation Density and Crystal Orientation on the Kinetics of the Catalyzed Oxidation of Ethylene Over a Single Crystal of Silver

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A study of the effects of dislocation density and crystal orientation on the kinetics of the catalyzed oxidation of ethylene to carbon dioxide over a single crystal of silver was carried out in a continuous-flow microreactor. A feed composition of approximately 20% ethylene and 80% oxygen was used for all reactor runs, and the temperature was varied from 250 to 350°C at atmospheric pressure. The dislocation density was increased by introducing a strain of 0.8% in the crystal, and the crystal orientation was chosen by adopting as the catalytic surface either the (100), (110), or (111) crystal plane. Results indicated that the crystal orientation had essentially no effect on the reaction rate but that straining the crystals caused a significant decrease in the rate. At 260°C and a total pressure of 740 mm Hg for a reactant mixture of nominally 20% ethylene and 80% oxygen, the rate of production of carbon dioxide was 5.6×10^{-8} mol/min cm^2 for the non-strained crystals and 2.8×10^{-8} mol/min cm^2 for the strained crystals. The conclusion is that dislocations do not act as active sites for the oxidation of ethylene to carbon dioxide but effect a change in the nature of the chemical structure of the surface to reduce the rate of oxidation.

INTRODUCTION

The oxidation of ethylene over a silver catalyst has been studied by various authors (*1–9*) using a variety of reactant compositions and catalyst supports in the temperature range of 150–400°C and the pressure range of 0.2–20 atm. Oxygen concentrations have been from 1.5 to 90 mol %, ethylene from 0.6 to 60%, carbon dioxide from 0.1 to 90%, and ethylene oxide from 0.3 to 3%. Nitrogen has been the usual diluent. A typical catalyst has been 12% by weight of silver supported on an alundum carrier (*7*). Typically a total conversion of 68% of the ethylene with a selectivity of 52% to ethylene oxide has been achieved at 274°C with an oxygen concentration of 20% and an ethylene concentration of 4.7% (*4*).

Since the investigations by Twigg (*10, 11*), there has been general agreement that the oxidation of ethylene over silver takes place along two parallel reaction paths, one in which carbon dioxide is formed directly and another in which ethylene oxide is formed and may be further oxidized to carbon dioxide. The first step of the reaction mechanism suggested by Twigg was the dissociative adsorption of oxygen on the silver surface. Ethylene could then react with the adsorbed oxygen to form ethylene oxide, or it could react through short-lived intermediates to form carbon dioxide and water. The ethylene oxide formed could also be oxidized further to carbon dioxide and water.

Since Twigg presented his papers, there have been many other investigations of the reaction. In particular, there has been considerable discussion concerning the adsorption of oxygen on the silver catalyst. Twigg assumed the oxygen became dissociated upon adsorption, but others (*12*, *13*) have proposed mechanisms in which ethylene reacted with adsorbed molecular oxygen. In adsorption studies with isotopes of oxygen, Sandler and Durigon (*14*) found no evidence that indicated the existence of undissociated oxygen. They and Czanderna (*15*) did find, however, that oxygen was adsorbed in different binding states, and Flank and Beachell (*16*) and Mikami, Satoh, and Kobayashi (*17*) related the selectivity of the reaction to the different adsorption states; they concluded that the more strongly adsorbed oxygen lead to carbon dioxide and that the less strongly adsorbed oxygen lead to ethylene oxide. In their reviews, Voge and Adams (*18*) and Sachtler (*19*) cited evidence that oxygen was adsorbed on silver both as atoms and as molecules but that the amount of molecular oxygen was usually small. Nault, Bolme, and Johanson (*20*) added another dimension to the controversy. They took the view that the bulk adsorption properties of the surface were not necessarily those that characterized the behavior of the catalytically active areas. From their experiments and from the data of others they concluded that ethylene and carbon dioxide were strongly adsorbed on the active sites and that oxygen was only weakly adsorbed. On the other hand, the work of Mikami *et al.* (*17*) indicated that the adsorption of ethylene on oxygenated silver was unimportant if it existed at all, and they adopted the more generally held view that the reaction was effectively that of adsorbed oxygen with gaseous ethylene. It has been reported by various authors (*9*, *17*, *21*, *22*) that the reaction products—ethylene oxide, carbon dioxide, and water—inhibited the reaction. In fact, Mikami *et al.* concluded from their experiments that carbon dioxide was preferentially adsorbed on the most strongly adsorbed oxygen and thereby inhibited the formation of carbon dioxide and increased the selectivity of the reaction.

There have been several investigations of the effect of different crystal planes on the adsorption and reaction on the silver surface. Orzechowski and MacCormack (*4*) proposed that different crystal planes could have different values for the various rate constants involved in their proposed mechanism and that poisoning of some of these crystal planes would account for the slow processes which affected the activity and selectivity of the catalyst. Stable oxygen–silver bonds and organic deposits were suggested as possible poisons. Kummer (*23*) suggested that the adsorption of oxygen might be affected by the different spatial separations in the crystal lattice on different crystal faces and performed experiments to determine this effect. He compared the activity and selectivity of single silver crystals with that of a sheet of polycrystalline silver. No differences were detected between the single crystals and the polycrystalline sheet. Wilson *et al.* (*24*) investigated the effects of the crystallographic orientation of the catalyst by comparing the catalytic activity and selectivity of randomly oriented silver films evaporated onto the inside of a pyrex glass tube with the activity and selectivity of films which were oriented with the (110) crystal plane parallel to the glass surface. No differences in the catalytic activity or selectivity were observed, but examination of the structure of the film by low-angle electron diffraction showed that the (110) film would lose its orientation after exposure to the reacting gases for a few hours. Czanderna (*25*) also observed changes in the surface properties of a silver-powder catalyst following the reaction. In both cases the energy released by the oxidation of ethylene was thought to be sufficient to cause reorientation of the silver surfaces. However, Jaeger (*26*), from his experiments on the decomposition of formic acid on silver, concluded that the catalytic activity depended on the crystal orientation. Flank and Beachell (*16*) studied the effect of lattice spacing by using gold–silver alloys of different compositions as catalysts and concluded that the catalytic activity for the oxidation of ethylene depended on lattice spacing. The effect of lattice spacing in the gold–silver alloys cannot, however, be divorced from the electronic interactions between the metal atoms and the adsorbed species. In this regard the effect of lattice spacing in the alloy does not provide conclusive evidence of such an effect in catalysts of pure silver.

The effect of dislocations on the adsorption and reaction processes has also been a subject of interest and controversy since the development of methods of direct observation of dislocations. Hall and Rase (*27*) observed a considerable increase in the rate of catalytic dehydrogenation of ethanol on single crystals of lithium fluoride with an increase in dislocation density on the crystal surface. Sosnovsky (*28*) in his studies used single crystals of silver with the (100), (110), and (111) planes exposed, and he increased the dislocation density by a bombardment of the silver surface with argon ions. He studied the catalytic decomposition of formic acid over such surfaces, and from the increase in reaction rate with dislocation density he concluded that the reaction occurred at sites where dislocation lines intersected the surface of the crystal. Uhara *et al.* (*29*) related dislocations in silver to active sites by studying the effect of temperature on reaction rates. At the annealing temperature they observed a dramatic decrease in the rates of several reactions including the decomposition of formic acid, and they attributed this behavior to the disappearance of dislocations. Perkins (*30*) also studied the decomposition of formic acid on single crystals of silver subjected to large increases in dislocation density on the surface. He found, however, only a small increase in the rate of decomposition, and his measurement of the hydrogen overpotential area of the surface showed a corresponding increase in the surface area with dislocation density. He concluded that dislocations did not act as active sites. The findings of Bagg, Jaeger, and Sanders (*31*) and Jaeger (*26*) also contradicted the conclusions of Uhara *et al.* From their studies of the decomposition of formic acid over silver, they concluded that dislocations had no measurable influence on the rate of the reaction.

In the present investigation, single crystals of silver with one face exposed were used as catalysts for the study of the effect of crystal orientation and dislocation density on the rate of oxidation of ethylene. Bulk crystals were used in order to avoid the crystal reorientation experienced by Wilson (*24*) and Czanderna (*25*), and the (100), (110), and (111) crystal planes were employed as catalytic surfaces. In studying the effect of dislocations, crystal surfaces of the same orientations were used, but the dislocation density was increased by cold-rolling the crystals. The dislocation density was estimated by pit density observed after treatment with etching solution.

Although the reaction of greatest interest was the partial oxidation of ethylene, a quantitative determination of the rate of that reaction could not be made because of low selectivity and the catalytic activity of gold surfaces in the reactor. It was possible, however, to establish 20 percent as an upper bound on the selectivity. Consequently the predominant reaction was the oxidation of ethylene directly to carbon dioxide, and the results refer specifically to that reaction.

METHODS

Apparatus

Single crystals of silver for use as the catalyst were purchased from the Unimet Company. Each crystal had been grown in the form of a ½-in., right circular cylinder with a particular crystal plane perpendicular to the axis of the cylinder, and three orientations—(100), (110), and (111)—were obtained for the study. The crystals were reported by the manufacturer to have orientations within ±2° of that specified, and the cylinders had been cut into ½-in. lengths by the manufacturer using an electric spark-cutting device to minimize the strain introduced into the surfaces.

A continuous-flow reactor was designed to provide a system in which the fluid flow and diffusional processes would be amenable to analysis. A cross section of the reactor is sketched in Fig. 1, and a more detailed diagram of the gold reactor head is presented in Fig. 2. Ethylene and oxygen entered the reactor head separately through

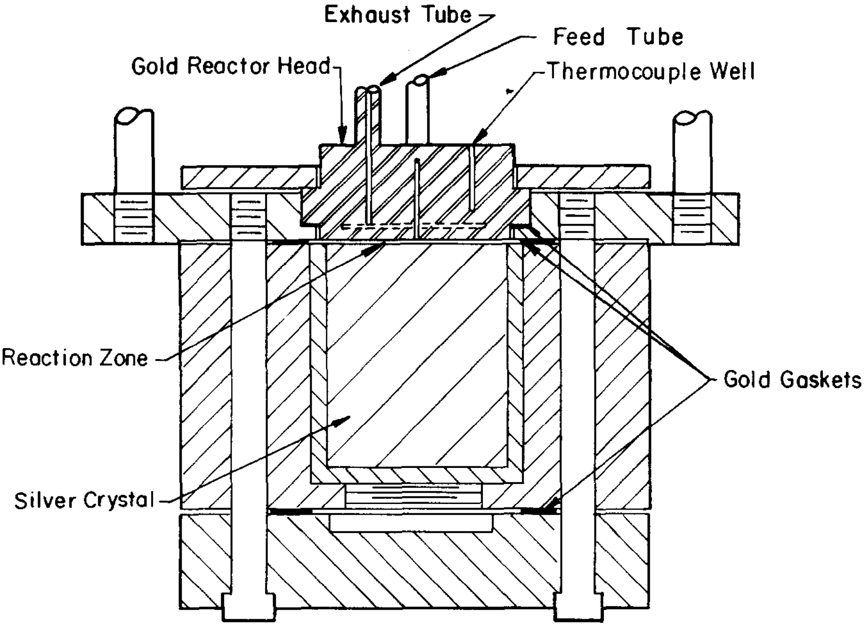

FIG. 1. Sectional view of reactor.

the two feed tubes. After mixing, they passed through a 0.01-in. hole in the center of the reactor head into the reaction zone. From there the gases flowed outward with radial symmetry through the 0.005-in. passage between the silver crystal and the bottom surface of the reactor head. From the periphery of the reaction zone they passed through the gold system and out the exhaust tube into the chromatographic detection unit. The gold discharge tube was placed in a water-cooled jacket to reduce the heated length of the tubes in order to minimize secondary reactions. Although gold was chosen as the material for the reactor head because of its low catalytic activity, the oxidation of ethylene and ethylene oxide on the gold surfaces was nevertheless significant.

In order to control its temperature, the reactor was placed in a bed of 60–80 mesh glass beads fluidized with heated air. The temperature was controlled to ±0.5°C and the rate of heat transfer within the bath was sufficiently great that the reactor remained only about 3°C below the bath temperature despite heat losses from conduction along feed tubes, exhaust tube, and reactor supports.

The volumetric flow rate of the exhaust gas was measured with a soap-film flow meter, and the composition was determined with gas chromatographs of high sensitivity. The unit consisted of three columns and three detectors. A hydrogen-flame detector was used for detection of the oxygenated reaction products, and a minimum detection limit of 5 ppm for ethylene oxide and acetaldehyde was obtained with a sample size of 1 cc. Each of the other two detectors had a tungsten filament mounted in a thermal conductivity cell. One was used to measure the light gases and the other to measure the light hydrocarbons and carbon dioxide. The minimum detection limit for carbon dioxide was 60 ppm.

Experimental

One crystal of each of the three crystallographic orientations—(100), (110), and (111)—was used as catalyst in the reactor in the non-strained state, and one each of the three orientations was used after being strained 0.8%. The crystals were strained by deforming the cylindrical crystals 0.004 in. on the 0.5-in. diameter by cold-rolling parallel to the axis of the crystal with a 3-in. hand roll. The rolling was repeated at

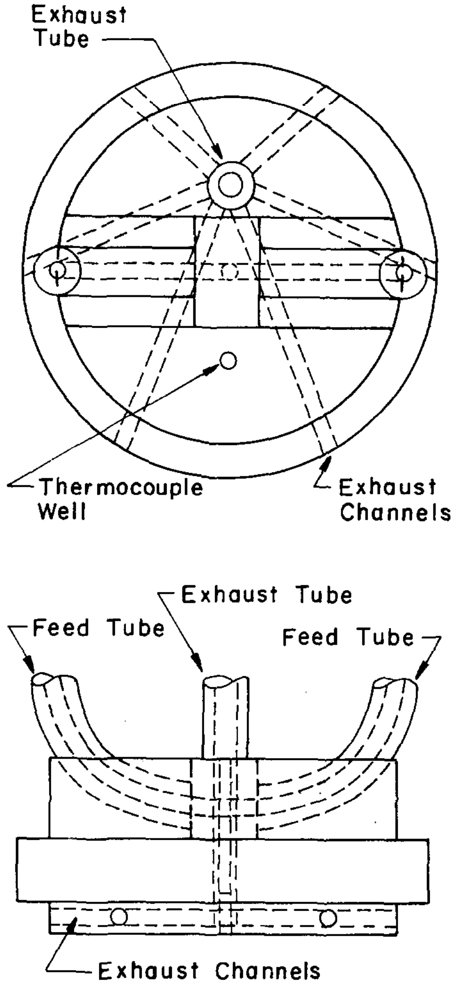

FIG. 2. Top and side views of reactor head.

45° increments around the circumference of the crystal. With this method of straining, some visible deformation over most of the face of the crystal occurred, but there was no loss in the general cylindrical shape of the crystal. The three nonstrained crystals and the three strained crystals were chemically polished by the method of Gilpin and Worzala (*32*), etched by the method of Levenstein and Robinson (*33*) to show the dislocation densities of the polished surfaces, photographed to record the dislocation densities, and repolished to remove the etch pits. These operations were performed on the six crystals at the same time in order to produce surfaces in the same condition for use as catalysts. The crystals were stored in a desiccator until needed for use in the reactor.

C. P. grade ethylene with a minimum purity of 99.0% was purchased from the Matheson Company for use as a feed gas to the reactor. Analysis of the ethylene showed that it contained at least ten hydrocarbon impurities. They were removed by passing the ethylene through two columns, each four feet in length with the 1.25-in. inside diameters filled, respectively, with Linde Type 5A and Linde Type 13X molecular sieve. The columns had been activated by heating at 250°C under vacuum for several days and were contained in a dry ice–acetone slurry during the purification operation. Purified ethylene was condensed in a liquid nitrogen trap and later boiled into a stainless-steel storage tank at a pressure of 80 psig. Ethylene obtained in this manner contained only about 1 ppm of an unsaturated C_4 hydrocarbon and about 1% nitrogen. A mixture of ethylene oxide in helium was prepared for use as a feed gas in determining the rate of oxidation of ethylene oxide on the gold surfaces of the reactor. Matheson ethylene oxide of 99.7% minimum purity was used in the mixture. No impurities were detected by gas chromatographic analysis of the ethylene oxide. Helium from Linde with a purity of 99.99% was used in the balance of the mixture. Oxygen of 99.5% minimum purity for the reactor feed was used directly from Linde cylinders with no further treatment.

A series of reactor runs was made with constant feed composition at atmospheric pressure while the temperature was changed between runs. A constant total-flow rate of about 1 cc/min at room conditions and a feed composition of about 20% ethylene and 80% oxygen were selected from the results given by Buntin (*7*) and Wan (*3*) to give an appropriate reaction rate. The temperature sequence used in the runs was 320, 350, 250, and 280°C and was adopted because of changes in catalytic activity that occurred after the reaction was begun over a clean crystal. When the initial temperature was 250 or 280°C, the activity was observed to increase during the reaction. The increase occurred slowly at 250°C and more rapidly at 280°C. At 320°C the change was presumably so rapid that the catalytic surface attained steady state before the concentration measurements were performed. Three samples of the reactor exhaust were taken at each reactor temperature. Each sample required about 30 min for analysis so the reactor remained at each temperature for at least 2.5 hr, including an hour at a new temperature before taking a sample. Concentrations of carbon dioxide in the exhaust varied from mole fractions of roughly 5×10^{-4} at 250°C to approximately 2×10^{-2} at 350°C.

Deposits were formed on the surfaces of the crystals used as catalysts. It was not possible to remove them with solvents such as methyl alcohol, ethyl alcohol, acetone, or ethylene dichloride, nor could they be removed by ultrasonic cleaning with hexane. The deposits were presumed to be carbanaceous complexes, and there appeared to be no relationship between the amount of deposit on the surface and the length of time the crystal remained in the reactor. Twigg (*10*) and Margolis (*34*) reported the development of an organic residue on the silver catalyst, and both found that it reached a constant state of development after which the catalytic activity became constant. It is probable that the change in catalytic activity observed at 250 and 280°C resulted from development of the deposit.

Since the reaction kinetics were not seriously investigated, the reaction rate was calculated simply by equating it to the production rate determined from the exhaust-gas measurements. The data of Klugherz and Harriott (*9*) showed, however, that even at low conversions the reaction products could have a significant inhibitory effect on the reaction rate. An analysis of the effect of product concentration on reaction rate would then require a detailed analysis of conditions within the reactor. Such an analysis was performed for the radial-flow reactor used in this work (*35*), and it showed that radial diffusion had a pronounced effect on the concentration profile of reaction products.

RESULTS AND DISCUSSION

Oxidation of Ethylene on Gold

In order to interpret the rate data obtained with the silver crystals, determination of the effect of the gold surfaces on the experimental results was necessary. The rate of oxidation of ethylene on gold was determined from a run in which the silver crystal was replaced by a gold disk. Variations in the feed concentration were insufficient to permit determination of the proper form for the rate expression, but analysis of the temperature dependence indicated the activation energy for the formation of carbon dioxide on the gold surface was in the range of 26.0 ± 4.0 kcal/mol. The total rate of production of carbon dioxide with the gold disk in the reactor was approximately 20 percent of the rate using a silver crystal.

Oxidation of Ethylene Oxide on Gold

The oxidation of ethylene oxide on gold was studied to determine the effect of the gold surface on the ethylene oxide produced on the silver catalyst. The feed-gas concentrations were approximately 0.03% ethylene oxide, 80% oxygen, and 20% helium, but the concentrations varied enough to show that the oxidation rate was independent of ethylene oxide concentration. The apparent activation energy was 9.0 ± 1.3 kcal/mol, and the reaction rate was comparable in magnitude to that of ethylene on gold. A comparison of reaction rates is presented in Table 1. Since oxygen does not adsorb on gold (*36*), the most obvious explanation for the zero-order dependence of

TABLE 1
PRODUCTION RATE OF CARBON DIOXIDE[a]

Reaction	Rate (mol min^{-1}cm^{-2})
$C_2H_4 \rightarrow CO_2$ on Ag (nonstrained)	5.6×10^{-8}
$C_2H_4 \rightarrow CO_2$ on Ag (strained)	2.8×10^{-8}
$C_2H_4 \rightarrow CO_2$ on Au	2.9×10^{-9}
$C_2H_4O \rightarrow CO_2$ on Au	2.1×10^{-9}

[a] Reactor conditions: 20% ethylene; 80% oxygen; temperature—260°C; pressure—740 mm Hg.

the rate on ethylene oxide concentration would involve the rapid adsorption of ethylene oxide on the gold surface. The rate-controlling step might be the reaction of gaseous oxygen with the adsorbed ethylene oxide. The adsorption of ethylene oxide is certainly plausible, since ethylene and carbon monoxide are known to adsorb on gold (*36*).

Oxidation of Ethylene on Silver

Because of reactions occurring on the gold surfaces, it was not possible to distinguish between oxidation to ethylene oxide and oxidation to carbon dioxide on the silver crystal. The concentration of ethylene oxide detected in the product gases was about 10 ppm, so essentially all of the reacted ethylene was converted to carbon dioxide. Although it was not possible to determine the selectivity, the reaction rate data did provide an upper limit. Comparison of the rate of oxidation of ethylene oxide on gold with the production rate of carbon dioxide on silver showed that the selectivity could not have been over 20%. The rate of production of carbon dioxide on silver was obtained from the reaction-rate data by subtracting the oxidation rate of ethylene on gold, and the resulting rate included the possible oxidation of ethylene oxide on gold. In addition to ethylene oxide, acetaldehyde was also detected as a product in concentrations of about 10 ppm for reactions over both silver and gold. Also, substances which were tentatively identified as C-4 and C-6 hydrocarbons were detected in concentrations of about 1 ppm.

Effect of Crystal Orientation and Dislocations

The rate data showed that the crystal orientation had essentially no effect on the reaction rate and that the rate decreased with an increase in dislocation density. These results are shown in the Arrhenius plots of Figs. 3, 4, and 5. In order to plot rate constants against temperature, it was necessary to choose a rate expression for the reaction on silver. Variations in feed concentrations were insufficient to determine the expression; so the reaction was assumed to be first order with respect to ethylene and half order with respect to oxygen. In any case, the Arrhenius activation energy is quite insensitive to the form of the expression. Although the graphs show

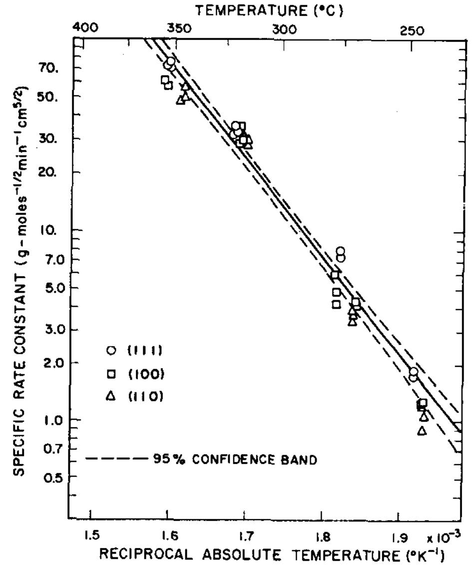

FIG. 3. Temperature dependence of rate constant for production of CO_2, combined fit for nonstrained crystals, ethylene order: 1: oxygen order: 1/2.

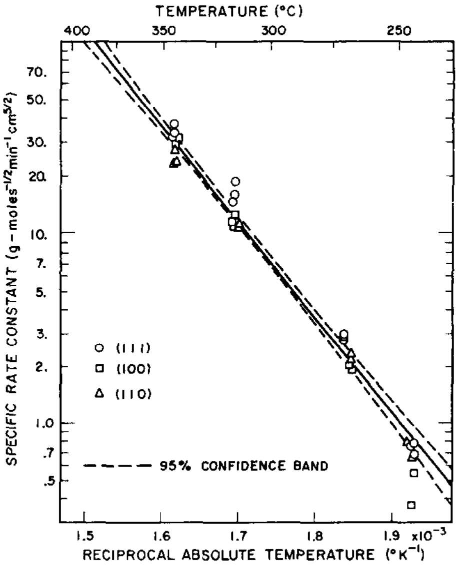

FIG. 4. Temperature dependence of rate constant for production of CO_2, combined fit for crystals strained 0.8%, ethylene order: 1: oxygen order: 1/2.

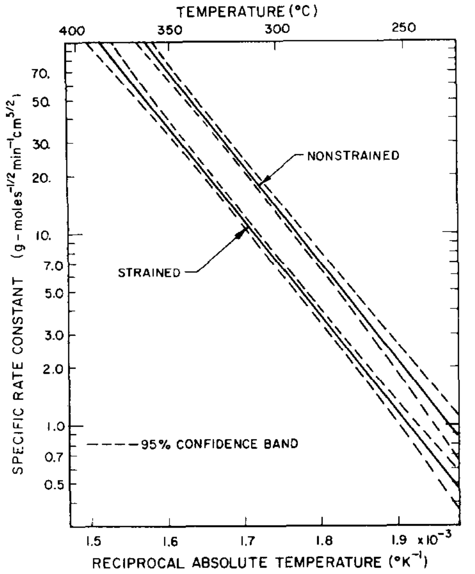

FIG. 5. Comparison of combined fits for strained and nonstrained crystals.

some ordering of the data according to crystal orientation, this effect lies within the range of experimental error and is not statistically significant. The strained crystals gave a significantly lower reaction rate than did the non-strained crystals, but the activation energies were the same. This result implies that dislocations did not act as active sites for the oxidation of ethylene but interfered with the reaction perhaps by binding the oxygen so tightly as to render it unavailable. It is possible that the extra atoms available for bonding at dislocations resulted in stronger bonds. The reaction rate and activation energy determined in this study are compared with the results of others in Tables 2 and 3. Combination of the estimated errors in all the variables used for the calculation of the rate constants gave an expected error of 10% for runs with relatively high conversions and an error approaching 40% for runs with carbon dioxide concentrations near the minimum detection limit. Scatter in the experimental values of the rate constants was approximately equal to the expected uncertainty.

TABLE 2

COMPARISON OF REACTION RATES[a]

	Rate of disappearance of ethylene (mol min^{-1}cm^{-2})
Buntin (*7*)	1.3×10^{-8}
Orzechowski and MacCormack (*4*)	6.5×10^{-8}
Wan (*3*)	1.0×10^{-8}[b]
This work, nonstrained crystals	2.8×10^{-8}
This work, strained crystals	1.4×10^{-8}

[a] Reactor conditions: 20% ethylene; 80% oxygen; temperature—260°C; pressure—740 mm Hg.

[b] Based on an assumed value of specific surface area of 1 m^2/g.

Etch Pits on Silver

The assumption of a one-to-one correspondence of etch pits to intersections of dislocations with the crystal surface, particularly for the crystals after use in the reactor, was considered somewhat questionable. There were difficulties in distinguishing etch pits from the background pattern on the surfaces, and there were changes in the shapes of the etch pits on the surface after use in the reactor. The changes could have been caused by physical changes in the surface of the crystals or by introduction of impurities into the crystals during use in the reactor. The polishing step, which was necessary to prepare the crystals for etching after use in the reactor, removed about 0.001 in. of metal. It seems improbable that physical changes produced by reaction could have extended so deeply into the crystal when 77-eV argon ions used by Sosnovsky (*28*) only produced

TABLE 3

COMPARISON OF ACTIVATION ENERGIES FOR PRODUCTION OF CARBON DIOXIDE

	Activation energy (kcal/mol)
Buntin (*7*)	15.0
Kummer (*23*)	22.9
Orzechowski and MacCormack (*4*)	20.3
Twigg (*10*)	10.0
Wan (*3*)	19.3
This work	23.0

TABLE 4
ETCH-PIT DENSITIES

Crystal	Density (pits/cm^2) Before reaction	Density (pits/cm^2) After reaction
(100), Nonstrained	5.1×10^6	2.1×10^7
(100), Strained 0.8%	6.8×10^6	6.1×10^6
(110), Nonstrained	Did not etch	Did not etch
(110), Strained 0.8%	Did not etch	Slight pitting
(111), Nonstrained	2.9×10^6	7.2×10^6
(111), Strained 0.8%	4.2×10^6	Few definite pits

physical changes to a depth of 100 Å. The introduction of impurities is considered a more probable explanation. Regardless of the relationship between etch pits and dislocations, there was a significant difference between strained and nonstrained crystals in their effects on the oxidation of ethylene to carbon dioxide. Measurements of the etch-pit densities are recorded in Table 4.

CONCLUSIONS

1. The orientation of the crystal planes parallel to the catalyst surface did not significantly affect the rate of production of carbon dioxide from ethylene and oxygen on silver.

2. The rate of oxidation of ethylene on silver was significantly reduced by straining the crystal prior to use as a catalyst. The activation energy of 23.0 kcal/mole for the reaction was not affected by a strain of 0.8% in the crystal. This result implies that dislocations did not act as active sites for the reaction probably because of their strong bonding of oxygen.

3. Deposits formed on the catalyst surface and reached a constant state of development during use in the reactor. The increase in reaction rate, presumably during the development of the deposit, suggests that the deposit contributed to the catalytic action of the surface.

4. Changes in the pitting of the crystal surfaces by the etching solution were observed after the crystal was used in the reactor. The changes could have been caused by physical changes in the surface of the crystals or by introduction of impurities into the crystals during use in the reactor, the latter reason seeming more probable.

5. Analysis of reactions on the gold surfaces placed an upper limit of 20% on the selectivity for ethylene oxide of the reaction on the silver crystals. Furthermore, the rate of oxidation of ethylene oxide on gold with feed-gas concentrations of approximately 0.03% ethylene oxide, 80% oxygen, and 20% helium was found to be independent of ethylene oxide concentration.

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