JOURNAL OF CATALYSIS **94**, 436–444 (1985)

The Selective Epoxidation of Ethylene Catalyzed by Ag(111): A Comparison with Ag(110)

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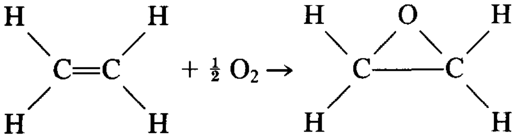
Received December 29, 1984; revised March 19, 1985

The kinetics of selective ethylene oxidation catalyzed by a clean Ag(111) surface have been measured at medium pressures. Using an apparatus that allows rapid transfer of the catalyst from the reactor into ultrahigh vacuum, the surface condition immediately (<17 s) after steady-state reaction has been analyzed by AES, LEED, XPS, and TDS. These results are compared with those on Ag(110) and supported Ag catalysts. The effects of temperature and reactant pressures upon the reaction rates are the same for these. The activity of Ag(111) in epoxidation is about half that of Ag(110) (per cm^2), but ~50 times higher than reported results for high-surface-area Ag catalysts. The steady-state coverage of atomically adsorbed oxygen is a factor of about 18 lower on Ag(111) than on Ag(110). These results are consistent with a mechanism whereby molecularly adsorbed O_2 and ethylene combine to form an intermediate in the rate-determining step. This intermediate then rapidly branches into ethylene epoxide or CO_2 pathways.

I. INTRODUCTION

The selective oxidation of ethylene to ethylene epoxide



is a large industrial process, typically performed over a silver catalyst supported on α-Al_2O_3 of ~1 $m^2 \cdot g^{-1}$ specific surface area. We have recently completed extensive studies of the kinetics and mechanism of this reaction over a clean Ag(110) single-crystal surface (*1, 2*). We found that the variation in the reaction rates and selectivity with reactant pressures (P_{O_2},P_{Et}) and temperature were virtually identical on Ag(110) and high-surface-area, supported Ag catalysts (*1, 2*). However, the *absolute* reaction rates (per surface Ag atom) were some two orders-of-magnitude larger on Ag(110) than for those that have been reported for high-surface-area catalysts (*2*). This suggested that perhaps the activity of real catalysts was due to a small fraction of (110)-like sites. The (111) plane is thought to predominate on the surface of real catalysts, due to its thermodynamic stability. The present study was initiated to verify the low activity of this (111) plane. Instead, we found that its activity is only a factor of 2 below the (110) plane. This indicates that the reported rates for high-surface-area Ag catalysts may be in error, perhaps due to inaccuracies in the Ag surface-area measurement.

II. EXPERIMENTAL

The techniques and equipment have been described in detail elsewhere (*1, 3*). In short, the Ag(111) or (110) surface was cleaned and characterized in ultrahigh vacuum (UHV) by XPS, AES, TDS, and LEED. The sample was translated into a microreactor. The reactor was pressurized with the reaction mixture. The sample was rapidly heated to and maintained at the reaction temperature for long enough to establish a steady-state reaction rate, as monitored by gas chromatography. Finally, the sample was rapidly (<17 s) translated back into UHV for postreaction surface analysis. We have shown (*1*) that the steady-state coverage (θ_O) of atomically adsorbed oxy-

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gen (O_a) under reaction conditions is maintained during this transfer, and that θ_O can be measured by thermal desorption spectroscopy (TDS).

Absolute coverages (θ) are defined relative to the number of Ag surface atoms. [$\theta = 1$ is 1.38×10^{15} cm^{-2} for Ag(111) and 8.5×10^{14} cm^{-2} for Ag(110).] Sample sizes were: Ag(111) = $10 \times 7 \times 2$ and $9.6 \times 5.6 \times 2$ mm for Ag(110). The sides and back of the crystals were passivated by a mixed Si, Cu, Ti oxide/carbide film (*1*). Thus the active geometric areas were 0.70 and 0.56 cm^2 for Ag(111) and (110), respectively. These surface areas were confirmed by detailed comparisons of the areas under the O_2-TDS peaks for known structures of atomically adsorbed oxygen (*4*). By the temperature differences in the oxygen desorption from these two planes (*4*), we also verified that less than ~2% of the (111) crystal surface consists of (110)-like defects (*4*). Thus our kinetics here are *truly* face specific.

III. RESULTS

The buildup of product concentration with time on Ag(111) in the batch microreactor was almost identical to that reported already (*1*) for Ag(110). A steady-state rate of epoxide production is established already in less than 30 s; and CO_2 production is very nearly steady state after 4 min. We have used 4 min reaction times. This corresponds to roughly 1000 molecules of ethylene converted to product per surface Ag atom. Total conversions are quite low ($\lesssim 5\%$). We will refer to steady-state rates here, as in our previous work (*1, 2*), as rates which are almost constant with time at these low conversions. The rates will, of course, decrease at very high conversions.

TABLE 1

Absolute Rate Comparison: Ag(111) vs Ag(110), per cm^2

Ag plane	T (K)	P (Torr)		TON_{EtO}[a]	TON_{CO_2}[a]	S_{EtO} (%)
		Et	O_2			
(111)	490	4.1	150	0.76	2.64	36.2
(110)				1.37	4.93	35.8
(111)	490	20	150	1.86	4.39	46.0
(110)				2.48	7.87	38.6
(111)	539	20	150	5.66	12.3	47.8
(110)				8.22	27.9	37.0

[a] TON in units of 10^{15} molecules produced · cm^{-2} · s^{-1}.

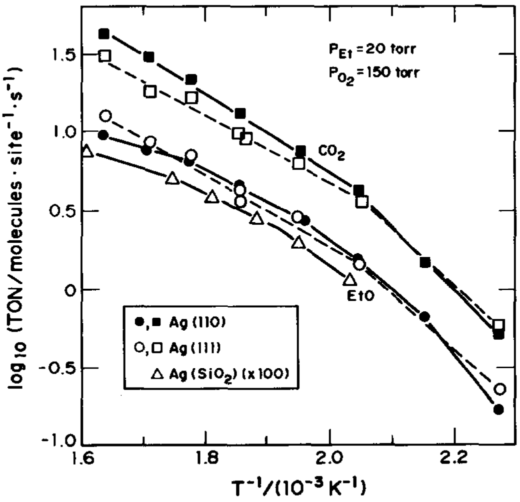

FIG. 1. Steady-state reaction rates of ethylene epoxide (EtO) and CO_2 production at 20 Torr ethylene and 150 Torr O_2, for Ag(111), Ag(110) (*1, 2*), and a supported silver catalyst of ~1 m^2 g^{-1} surface area (*5*).[1] TON refers to the turnover frequency.

Figure 1 compares the effects of temperature (in Arrhenius form) upon the steady-state reaction rates for both ethylene epoxide (EtO) and $CO_2(+H_2O)$ production over Ag(111), Ag(110) (*1, 2*), and a high-surface-area, supported Ag catalyst (*5*).[1] In Figs. 1–4, we have calculated the absolute reaction rates (TON ≡ molecules produced per second per surface silver atom or "site") by assuming 10^{15} sites for each crystal. This is slightly (factor of $\lesssim 2$) in error, but a true *absolute* rate comparison will be presented in Table 1. It is clear in Fig. 1 that the effect of temperature on catalytic activity is very

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[1] Silver surface area taken to be equal to the BET surface area. See Ref. (*2*) for justification.

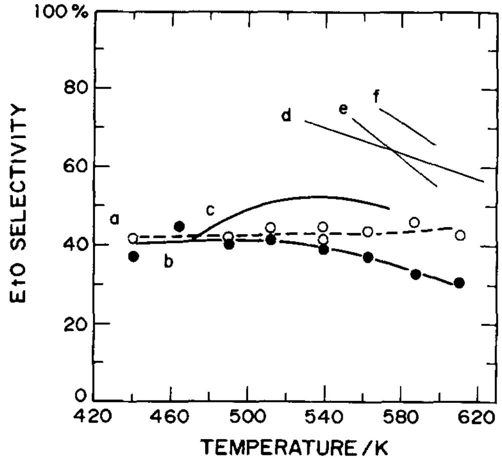

FIG. 2. Data of Fig. 1 for P_{O_2} = 150 Torr and P_{Et} = 20 Torr, replotted to show directly the effect of temperature upon the selectivity for ethylene conversion into EtO: (a) Ag(111), (b) Ag(110) (*2*), (c) Ag/SiO$_2$ (*5*). Also shown are selectivities at different pressure conditions for several high-surface-area Ag catalysts: (d) porous Ag (*7*), (e) Ag/Al$_2$O$_3$ (*8*), (f) Ag/SiO$_2$ (*8*).

nearly identical on these three very different Ag catalysts.

Figure 2 shows the data of Fig. 1 replotted to show directly the effect of temperature upon the selectivity for EtO production: $S_{EtO} = TON_{EtO}/(TON_{EtO} + \frac{1}{2} TON_{CO_2})$. The reader will note that the selectivity curve for Ag(110) falls slightly (~15%) below our previous values (*2*). The data used in this paper from our previous work (*1, 2*) is the same; it has simply been adjusted for a small error in gas chromatograph sensitivity calibration persistent in our previous work (*1, 2, 6*). This error resulted from an error in the standard gas mixture used for calibration. It has *no* bearing upon the conclusions of our previous work.

One can see in Fig. 2 that the selectivity for Ag(111) and (110) is in the range of ~42%, slightly below the widely scattered values for (presumably) unpromoted, high-surface-area silver catalysts (*5, 7, 8*). Ag(111) shows almost *no* variation in selectivity with temperature, while Ag(110) shows a slight decrease.

Table 1 compares absolute steady-state rates and selectivities under several conditions for Ag(111) and (110). These results are averages of several measurements made on two consecutive days, allowing little time for gas chromatograph drift. (No drift was observable using our calibrated standard gas mixture.) When compared on a "per cm^2" basis, Ag(111) is about a factor of 1.8 less active in EtO production than Ag(110). This difference is a factor of ~1.6 larger if a comparison is made on a "per surface Ag atom" basis. The selectivity for Ag(111) is 1–10% higher than on Ag(110).

Figure 3 compares the effects of O$_2$ pressure upon the rates, selectivity, and atomic oxygen coverage (θ_O) at 490 K and 4.1 Torr ethylene (Et) for Ag(111) and Ag(110) (*1*). Both the EtO and CO$_2$ production rates start out with high order in P_{O_2}, but eventually saturate in oxygen. There is very little difference between Ag(111) and (110) in this respect, except that CO$_2$ production saturates slightly more rapidly in P_{O_2} on

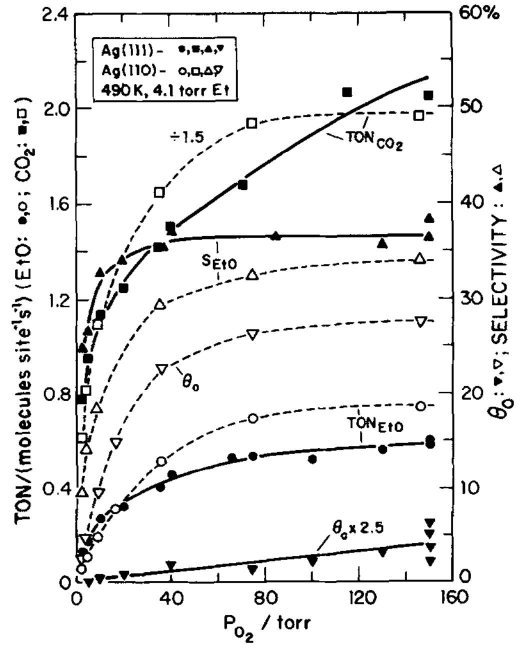

FIG. 3. Effect of oxygen pressure at P_{Et} = 4.1 Torr and 490 K upon the steady-state reaction rates, selectivity, and atomic oxygen coverage (θ_O) for Ag(111) and Ag(110) (*1*). Note that TON$_{CO_2}$ on Ag(110) has been divided by 1.5, and θ_O on Ag(111) multiplied by 2.5. Coverage units defined under Experimental.

Ag(110) than on Ag(111); and, EtO production saturates slightly more slowly. The atomic oxygen coverage is a factor of ~18 higher on Ag(110).

Figure 4 compares the effects of ethylene pressure upon the steady-state rates, selectivity and θ_O for Ag(111) with Ag(110) (*1*) at 490 K and 150 Torr O_2. Again, the rates start out high order in P_{Et} but eventually saturate in ethylene. The saturation in both rates occurs noticeably sooner on Ag(110) than on Ag(111). Again, the atomic oxygen coverage is a factor of 10–20 higher for Ag(110).

We confirmed with postreaction LEED analysis that the Ag(111) surface maintained a very sharp and bright $p(1 \times 1)$ LEED pattern immediately after reaction (transferring at reaction temperature into UHV, then immediately cooling for LEED analysis). Under conditions (high $P_{O_2} : P_{Et}$) where coverages of atomic oxygen $\theta_O \gtrsim 0.07$ were achieved at steady state, a faint but sharp $p(4 \times 4)$ LEED pattern was obtained. This pattern is characteristic of atomic oxygen in islands of local coverage $\theta_O \cong 0.41$ (*4*). The O_a on Ag(110) was existing during reaction in $p(2 \times 1)$ islands of local coverage $\theta_O = 0.5$ (*1*). The nature of the adsorbed oxygen species, measured by the area under the ~580 K O_2-TDS peak and plotted in Figs. 3 and 4, was also confirmed by AES and XPS peak positions and lineshapes. These agreed with those for atomically adsorbed oxygen on Ag(111) (*4*), as was also the case with Ag(110) (*1*). As with Ag(110) (*1*), AES revealed no significant surface species other than O_a present after transfer into UHV for reactions above 480 K.

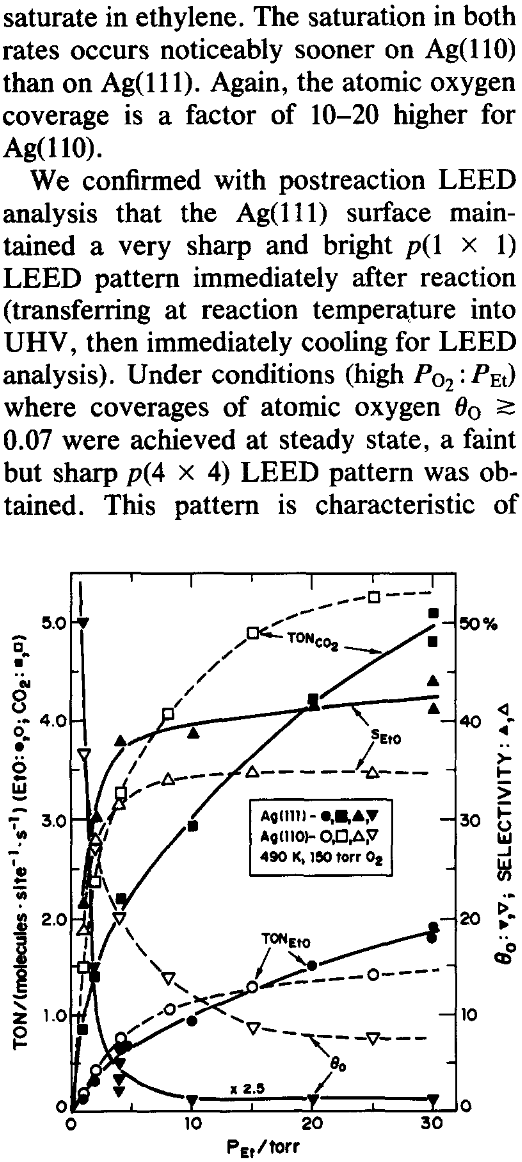

FIG. 4. Effect of ethylene pressure at 490 K and P_{O_2} = 150 Torr upon the steady-state reaction rates, selectivity, and atomic oxygen coverage (θ_O) for Ag(111) and Ag(110) (*1*).

IV. DISCUSSION

A single reaction mechanism has been consistent with our previous extensive kinetic data on Ag(110) of the type presented in Figs. 1–4 and of other types, particularly that related to the role of adsorbed chlorine in promoting selectivity (*1–3, 6, 9, 10*). This mechanism, in somewhat modified forms, had been previously proposed to explain more classical catalytic studies [(*11, 12*) and refs. therein]. This mechanism is summarized below, where the subscript "a" means "adsorbed" and no subscript implies "gas phase":

$$C_2H_4 \rightleftarrows C_2H_{4,a}, \tag{1}$$

$$O_2 \rightleftarrows O_{2,a}, \tag{2}$$

$$O_{2,a} \rightarrow 2O_a, \tag{3}$$

$$C_2H_{4,a} + O_{2,a} \xrightarrow[\text{RDS}]{\text{slow}} I_a, \tag{4}$$

$$I_a \xrightarrow{\text{Fast}} C_2H_4O + O_a, \tag{5}$$

$$I_a \xrightarrow{\text{Fast}} \text{Fragments}, \tag{6}$$

$$\text{Fragments} + 4O_a \rightarrow 2CO_2 + 2H_2O. \tag{7}$$

Here, the intermediate I_a is some C_2H_4/O_2 complex, formed in the rate-determining step (RDS) under most conditions. The rate of this step may be expressed as (*1, 9, 10*)

$$R_4 = \nu_4 \exp(-E_4/RT)\theta_{Et}\theta_{O_2}. \tag{8}$$

Kinetics on Ag(110) are consistent with a preexponential factor $\nu_4 \cong 10^{-2}$ cm^2 s^{-1} (*1*) and an activation energy $E_4 \cong 25$ kcal mol^{-1} (*1, 9*) for this step. The intermediate thus formed then rapidly branches into either the desirable product or fragments that yield $CO_2 + H_2O$. The coverage of I_a at steady state is therefore very small. The selectivity is determined by the branching ratio for this intermediate, *after* the RDS.

A second, minor pathway to CO_2 production seems to exist, involving dissociation of ethylene without step (4), and further reaction with O_a (*1, 10*).

The molecularly adsorbed species involved in the RDS (4) have been characterized by surface spectroscopies on Ag(110) [(*3, 13–17*) and refs. therein]. Adsorbed ethylene is bonded via π-electron donation with a heat of adsorption of ~8.9 kcal mol^{-1} (*1, 6, 13, 14*), increasing to ~10.7 kcal mol^{-1} in the presence of O_a [(*1, 6, 13, 14*) and refs. therein]. The molecularly chemisorbed $O_{2,a}$ is a peroxo-like species ($O^{2-}_{2,a}$) lying parallel to the surface, with a reduced O–O bond order near unity (*3, 14–17*). It has a heat of adsorption of ~9.3 kcal mol^{-1}, and an activation energy for adsorption of ~1.5 kcal mol^{-1} (*4*).

The present data for Ag(111) are consistent with the above mechanism. The bonding of ethylene to the Ag(111) surface (*18*) is quite similar to that for Ag(110), and it appears to have about the same heat of adsorption on these two surfaces. This is consistent with the rather minor kinetic differences with respect to P_{Et} seen for these two surfaces (Fig. 4).

The interaction of O_2 with these two surfaces has recently been compared in detail (*4*). The atomically adsorbed state has a heat of adsorption, ΔH_a^A, of only 40.8 kcal mol^{-1} on Ag(111), compared to 44.0 kcal mol^{-1} on Ag(110). Oxygen has a much lower dissociative sticking probability at 490 K on Ag(111) (~10^{-6}) as compared to Ag(110) (~2×10^{-4}). This difference feeds directly into the steady-state O_a coverage under reaction conditions, leading to a value θ_O that is a factor of ~18 lower on Ag(111) compared to (110) (Figs. 3 and 4). Note, however, that this large difference is *not* strongly reflected in the rates of ethylene oxide or CO_2 production. This is because, according to the mechanism above, O_a is not involved in the rate-limiting step. It is the coverage of $O_{2,a}$ (θ_{O_2}) that is critical here, not that of O_a.

Molecularly chemisorbed O_2 has a heat of adsorption, ΔH_a^M, of ~9.3 kcal mol^{-1} on both Ag(111) and (110), although the activation energy for its desorption, E_d^M, is significantly larger on Ag(111) (12.4 compared to 10.8 kcal mol^{-1}) (*4*). This is related to the larger activation energy for its formation, E_a^M, on Ag(111) (~3.2 kcal mol^{-1}) compared to Ag(110) (~1.5 kcal mol^{-1}). This barrier results in a low sticking probability into the molecularly chemisorbed state: 5×10^{-6} on Ag(111) and 7×10^{-4} on Ag(110) at ~140 K (*4*). At high temperatures and low coverages when adsorption/desorption equilibrium in $O_{2,a}$ is established, its coverage can be approximated by (*4*)

$$\theta_{O_2} = 0.25 fc/\nu_d^M \cdot \exp(\Delta H_a^M/RT), \quad (9)$$

where fc is the frequency of collisions of O_2 molecules with the surface (proportional to P_{O_2}) and ν_d^M is the preexponential factor for $O_{2,a}$ desorption (~10^{13} s^{-1} (*4*)). Since ΔH_a^M is about the same (~9.3 kcal mol^{-1} (*4*)) on Ag(111) and (110), this predicts that the steady-state coverages of $O_{2,a}$ on these two surfaces will be about the same. This is consistent with the rather minor kinetic differences seen with respect to P_{O_2} for these surfaces in Fig. 3.

The reaction rates in Fig. 3 at 490 K saturate in P_{O_2} at about 100 Torr. According to the rate-limiting step (4) in the proposed mechanism, this should occur at a coverage θ_{O_2} of around 50% of its saturation value. (Sites must remain on the surface for $C_2H_{4,a}$.) Similarly, at 5 Torr O_2 the rates are still first order in P_{O_2}, suggesting that θ_2 is only a few percents of its saturation value. Equation (9) predicts coverages θ_{O_2} of ~6 and ~0.3% (of the saturation values (*4*)) for

P_{O_2} = 100 and 5 Torr, respectively. These differ by a factor of about 8 from those suggested above by applying the proposed mechanism to the kinetic data of Fig. 3. Given the approximations inherent here, especially when extrapolating the low-temperature TDS results up to 490 K in Eq. (9), this agreement is good. (Note that an error of a factor of 13 in our original assumption that $\nu_d^M = 10^{13}$ s^{-1} (*4*) would correct this difference.) Thus, the range over which the rates saturate in P_{O_2} is consistent with the saturation of molecularly chemisorbed O_2, when one uses the kinetic parameters for O_2 absorption/desorption obtained from low-temperature TDS experiments on Ag(111) and (110). One can obtain similar agreement for a similar treatment of the extent of saturation in P_{Et} from the data of Fig. 4. Here we use an equation analogous to Eq. (9) for adsorbed ethylene and the heat of ethylene adsorption of 10.7 kcal mol^{-1} from TDS on Ag(110) in the presence of O_a (see above). Reference (*1*) presents related calculations at different temperatures. We should note that these species ($O_{2,a}$ and $C_2H_{4,a}$) desorb very rapidly at the reaction temperature and therefore are *not* available for postreaction surface analysis in UHV. Nevertheless, the high gas-phase pressures of O_2 and Et maintain their coverages high under reaction conditions.

It is interesting to note in Fig. 4 that the rates saturate somewhat more rapidly in P_{Et} on Ag(110) than on Ag(111). This indicates a slightly higher heat of adsorption for ethylene on Ag(110). This may simply be a consequence of its higher atomic oxygen coverage. The presence of O_a on Ag(110) can increase this heat of adsorption for ethylene by up to 1.8 kcal mol^{-1} [(*6, 13, 14*) and refs. therein].

The EtO production rate saturates more rapidly in P_{O_2} on Ag(111) than on Ag(110) (Fig. 3). This would suggest that $O_{2,a}$ is bonded slightly more strongly to Ag(111) than (110). Interestingly, the reverse is seen in CO_2 production: its rate saturates sooner in P_{O_2} on Ag(110). This may be due to the presence of the second, minor pathway to CO_2 mentioned above. This pathway seems to be of greater importance on Ag(110), which is consistent with its generally lower selectivity.

From Table 1, we can conclude that the (110) plane of Ag is a factor of about 2 more active than the (111) plane in catalytic ethylene epoxidation. This agrees well with recent results of Hagen (*19*), who has further shown that the (100) plane is some 15% more active (per cm^2) than the (110) plane in EtO production. Our absolute rates for Ag(111) and (110) agree with Hagen's results to within a factor of about 2.

We have shown that the specific activity for EtO production on Ag(110) is some two orders-of-magnitude higher than that reported for high surface area, supported Ag catalysts (*2*). Originally, we had postulated that this could be due to an unusually high activity on the (110) plane, existing only in small fraction on the surfaces of supported catalysts (*2*). (The (111) plane is the thermodynamically preferred surface.) We can now see, however, that such large activity differences do *not* exist between the various crystal planes of Ag. We must find an alternative explanation for the large (factor of ~50) difference in apparent activities for clean single-crystal surfaces and high-surface-area Ag catalysts.

The major source of error in determining absolute rates (per surface Ag atom) on high-area Ag catalysts involves determination of the number of free Ag surface atoms. This is usually accomplished by measuring oxygen chemisorption at ~470 K and ~50 Torr, and assuming one oxygen adatom per free surface Ag atom. There are two potential errors in this method, each of which could lead to substantial (factor of ~7) overestimates. First, any carbonaceous residue on the Ag will be oxidized to CO_2, creating free sites on the surface for O_a. These are sites that were unavailable for the epoxidation reaction under catalytic conditions. After extended operation, it is possible that a substantial portion of the Ag area of real catalysts is covered by such residue. Second, we have recently found (*20a*) that certain surface impurities, such as adsorbed chlorine, do not significantly decrease the oxygen chemisorption capacity of silver (under these adsorption conditions). However, the same coverage of these impurities can decrease the epoxidation rate by a factor of 10 (*6, 9*). Together, we feel that these impurity-related problems could lead to overestimates in the free Ag surface area by a factor of ~50 on high-surface area catalysts, resulting in an underestimate in the specific activity by this same factor. A further problem may be that rates on high-area catalysts tabulated in (*2*) were sometimes those after hours of operation (although initial rates were used where available). The rates generally decrease by a factor of 1.5 to 10 in 5 h of operation, depending on the catalyst (*20b*).

This reaction has long been known to be classically structurally sensitive; i.e., the rates and selectivity depend sensitively upon the size and shape of Ag particles in high-surface-area catalysts (*21–25*). However, in light of the present results and those of Hagen (*19*), these large rate variations apparently cannot be related to variations in the concentration of active surface facets with particle size. It may be that some impurity from the preparation process or support material poisons the catalyst surface, and the concentration of this poison is dependent upon the same factors in the preparation scheme that allow for particle size adjustment. Three further facts might support this hypothesis: (1) a strange minimum in specific activity with particle size is observed at the surprisingly large size of 500–700 Å (*24*); (2) the variations in specific activity with particle size observed by any given author are smaller than the variations among authors for catalysts of nominally the same particle size (see Table I in (*2*)); and (3) the specific activities of unsupported, high-area Ag catalysts are at the upper limit of activities seen for high-area catalysts, and only a factor of about 5 below those for Ag(111) (see Table I in (*2*)).

For small particles, selectivity increases with particle size (*23, 25*). In our results, Ag(111) has an average selectivity that is about 6% higher (in absolute units) than Ag(110). Since the particle surface should evolve from open, or (110)-like, to close-packed, or (111)-like, with increasing size, these results may be favorably correlated. Since decomposition steps are crucial in both pathways to CO_2 production, it is not surprising that the (110) plane is relatively more active for CO_2 production than Ag(111). More open surface structures are typically more active in bond-breaking reactions. The second, minor pathway to CO_2 production involving ethylene dissociation is less important on Ag(111) than on Ag(110). In fact, the total independence upon temperature of the selectivity on Ag(111) in Fig. 2 seems to indicate that essentially *all* EtO and CO_2 production occurs through the same rate-determining step (4), and that the branching ratio (k_5/k_6) is temperature independent.

Note in Fig. 2 also that the selectivities for Ag(111) and (110) are noticeably lower than those reported for high-surface-area Ag catalysts. From our above discussion, it appears that considerable impurity may exist on the surfaces of the high-area catalysts under reaction conditions. These impurities may also effect selectivity [(*6, 9, 20*) and refs. therein]. Clearly, the surface condition of high-area silver catalysts during (or immediately after) steady-state reaction is an issue of importance that still must be addressed.

We should point out that the mechanism we have used to explain our data is by no means universally accepted. Particularly, one school of thought maintains that atomically absorbed oxygen is responsible for ethylene oxide production [(*26–28*) and refs. therein]. For reviews of mechanistic considerations in this reaction, see (*29–32*). We have chosen to reject mechanisms involving O_a for the following reasons. Under conditions where the EtO and CO_2 production rates are first order in P_{O_2} (for example, $T = 490$ K, $P_{Et} = 4.1$ Torr, $P_{O_2} = 8.2$ Torr), the rate-determining step must be the adsorption of oxygen into that state involved in the catalytic reaction. However, the addition of 0.3 monolayer of chlorine to Ag(110) hardly changes the kinetics under these conditions (*6*), in spite of the fact that this chlorine decreases the rate of dissociative O_2 adsorption by a factor of 20 (*6*). Similarly, our present data show that clean Ag(111) and Ag(110) have about the same epoxidation rates under these conditions, while the dissociative adsorption rate of O_2 on Ag(111) is a factor of 50 slower than on Ag(110) (*4*). Our measurements of θ_O after reaction (Ref. (*6*) and this work), confirm that these differences in dissociative oxygen adsorption rate (due to adding chlorine or changing the crystal face) are indeed qualitatively valid under reaction conditions. That these differences are *not* reflected in the epoxidation rate under oxygen-limiting conditions implies that dissociatively adsorbed oxygen is not involved in the rate-determining step. As noted above and in (*9*), molecularly chemisorbed oxygen does not suffer this same problem and is therefore a preferable choice as the oxidizer. Note that, at 490 K, molecularly chemisorbed oxygen on Ag(110) or (111) has a very low probability of dissociating rather than desorbing, so that the rate of dissociative adsorption is much lower than the rate of molecular chemisorption (*4*).

In our opinion, the evidence which argues most strongly in favor of a mechanism involving O_a is that of Backx *et al.* (*28*). These authors adsorbed oxygen on a silver powder, evacuated it at 470 K to remove any molecular O_2 but not O_a, then heated this surface from room temperature to ~415 K in 0.75 Torr Et. They found that >11% of the initial oxygen could be converted into ethlyene oxide in this manner. However, this result is not totally conclusive, since large coverages of coadsorbed ethylene (or surface carbonate from the CO_2 product) could force O_a to associatively recombine, forming O_2 at significantly lower temperatures than those required in the absence of these other adsorbates. Examples of such displacement reactions are not uncommon in the chemisorption literature (*33, 34*).[2] Another possibility for the discrepancy between this and our present results is that, while the mechanism observed by Backx *et al.* (*28*) is one possible pathway, it is not the dominate mechanism under steady-state reaction conditions.

Grant and Lambert (*26, 27*) have recently attempted a modified form of the Backx (*28*) experiment on a Ag(111) single crystal. Their results, however, are much less conclusive since only one EtO molecule was observed for every ~200 surface silver atoms. This minor amount could be due to a number of effects unrelated to the majority of the Ag surface. Spath (*35*), for example, saw *no* EtO product from this same experiment on high-area Ag unless molecular O_2 was present. Clearly, however, there is still controversy over the reaction mechanism.

V. CONCLUSIONS

The variation in reaction rates with temperature and pressure are virtually identical on Ag(111), Ag(110), and supported Ag catalysts. The specific rates (per surface Ag atom) are in the ratio 50 : 100 : 1 for these catalysts. The rates on supported Ag catalysts may be low due to incorrect Ag surface area calibration. The coverage of atomically adsorbed oxygen on the Ag(111) surface under steady-state reaction conditions is a factor of ~18 lower than on Ag(110), consistent with its lower dissociative sticking probability for O_2. The O_a resides in $p(4 \times 4)$ islands of local coverage $\theta_O = 0.41$. These results support a mechanism whereby molecularly adsorbed O_2 and ethylene combine in the rate-limiting step.

[2] Adsorbed CO desorbs at 100 K lower temperature from Rh(111) in the presence of NO (*34*).

This mechanism implies that the coverages of $O_{2,a}$ and $C_2H_{4,a}$ under reactions conditions on Ag(111) are very similar to Ag(110). This is consistent with TDS results at low temperature for these species.

ACKNOWLEDGMENT

The author wishes to gratefully acknowledge the valuable technical assistance of Johnny Anderson.

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