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TITLE: A SURFACE SCIENCE STUDY OF SELECTIVE ETHYLENE EPOXIDATION CATALYZED BY THE Ag(110) SURFACE: STRUCTURAL SENSITIVITY

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SURFACE SCIENCE STUDIES OF SELECTIVE ETHYLENE EPOXIDATION CATALYZED BY THE Ag(110) SURFACE: STRUCTURAL SENSITIVITY

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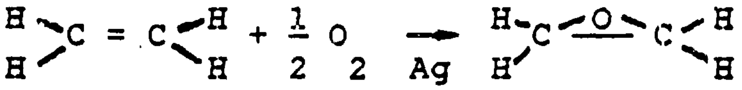
ABSTRACT

The selective oxidation of ethylene to ethylene epoxide ($C_2H_4 + 1/2\ O_2 \rightarrow C_2H_4O$) over Ag is the simplest example of kinetically-controlled, selective heterogeneous catalysis. We have studied the steady-state kinetics and selectivity of this reaction for the first time on a clean, well-characterized Ag(110) surface by using a special apparatus which allows rapid (~20 s) transfer between a high-pressure catalytic microreactor and an ultrahigh vacuum surface analysis (AES, XPS, LEED, TDS) chamber. The effects of temperature and reactant pressures upon the rate and selectivity are virtually identical on Ag(110) and supported, high-surface-area Ag catalysts. The absolute specific rate (per Ag surface atom) is however some 100-fold higher for Ag(110) than for high-surface-area catalysts. This is related to the well-known structural sensitivity of this reaction. It is postulated that a small percentage of (110) planes (or [110]-like sites) are responsible for most of the catalytic activity of high-surface-area catalysts. The high activity of the (110) plane is attributed to its high sticking probability

for dissociative oxygen adsorption, since the rate of ethylene epoxidation is shown in a related work [1] to be proportional to the coverage of atomically adsorbed oxygen at constant temperature and ethylene pressure.

I. INTRODUCTION

The selective oxidation of ethylene to ethylene epoxide (also known as ethylene oxide)



is catalyzed industrially using a silver catalyst supported on $\alpha - Al_2O_3$ of about $1 m^2 g^{-1}$ specific surface area. Enhanced selectivity is achieved by adding trace amounts of chlorinated hydrocarbons to the reactant feed. (The undesirable side product is $CO_2 + H_2O$.) This reaction is the basis of a several-billion-dollar per year industry, and it is the simplest prototype of the entire class of kinetically-controlled, selective heterogeneous catalytic reactions. It has been the subject of considerable fundamental research [2-22], although a great deal concerning the reaction mechanism and the nature of the active catalyst surface remains under question. More extensive data of the type we have presented here will appear in another paper, which deals specifically with the reaction mechanism over Ag(110) [1]. For the first time in that work, the steady-state reaction rates were measured not only as a function of temperature and reactant pressures, but also as a function of the coverage of atomically adsorbed oxygen, θ_O. A mechanism consistent with these data and with data from the literature was developed which involves two pathways for CO_2 production and a single pathway for ethylene epoxide (EtO) production. The path to EtO and one of the paths to CO_2 involves ethylene, adsorbed on $Ag^{\delta+}$ sites created by adsorbed atomic oxygen, and molecularly adsorbed O_2. The other path to CO_2 involves dissociated ethylene and atomically adsorbed oxygen, O_a.

The focus of the present work is a comparison between the specific activities and kinetics measured on Ag(110) and a variety of relatively high-surface-area Ag catalysts in an attempt to understand the well-known structural sensitivity of Ag catalysts in this reaction. It is a classical structural sensitive reaction: the specific reaction rates (per Ag surface atom) and selectivity depend strongly upon the average Ag cluster size (50-5000 Å) on supported catalysts [4-8]. Very early attempts to compare the catalytic activity of various crystal faces [15,16] or oriented Ag films [14] have indicated no large differences, although these studies were far from conclusive due to the absence of any surface analysis and the potential for surface re-orientation [5,14].

II. EXPERIMENTAL

The Ag(110) preparation technique is described in another paper [23]. Details of the apparatus and technique are presented in a related paper [1]. In short, the Ag(110) sample was cleaned by sputtering and annealing in ultrahigh vacuum (UHV), and its cleanliness and order were proven by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). The clean sample was transferred into an evacuated microreactor attached directly to the UHV chamber, pressurized with the reaction mixture (~200 torr) and heated (440-610 K) until a steady-steady epoxidation rate (2-4 min) was established. Then the sample was rapidly (17 s) transferred at reaction temperature back into UHV for surface analysis (AES, LEED, TDS, XPS). After transfer, the reaction mixture (still in the microreactor) was analyzed by gas chromatography for the amount of EtO and CO_2 produced. As discussed in a related paper [1], above 480 K the surface contained only atomically adsorbed oxygen and maintained a good LEED pattern after reaction. Below 480 K other adsorbed reactants and products were observed. The sides and back of the crystal were passivated to reaction by a mixed Si, Cu, Ti oxide/carbide film which built up during the early stages of high-pressure reaction attempts.

III. RESULTS

Figure 1 shows the steady-state rates of EtO and CO_2 production as a function of temperature, in Arrhenius form, at an ethylene pressure (P_{Et})of 20 torr and P_{O_2} = 150 torr on clean Ag(110). These specific rates in Figs. 1 and 3 are expressed in terms of the turn-over-number (TON), i.e., the number of molecules of each produced <u>per Ag surface atom</u> (site) per second, assuming 10^{15} Ag surface atoms on our sample. As pointed out previously, this probably underestimates the true TON, since our clean (110) surface area had only about 5 x 10^{14} Ag surface atoms [1]. Shown for comparison is the specific rate of EtO production over a high-surface-area, silica-supported Ag catalyst under the same conditions. (Note that the rate is multiplied by 100 for easier comparison.)

The activation energy for EtO production decreases from about 22.4 to 5.3 kcal mole^{-1} as the temperature increases from 440 to 610 K on Ag(110), almost identical to the behavior on the supported Ag catalyst. The activation energies for EtO and CO_2 production are very similar on Ag(110), again in agreement with high-surface-area catalysts [3,17].

The selectivity for ethylene conversion into EtO ($S_{EtO} = TON_{EtO}/[TON_{EtO} + 1/2\ TON_{CO_2}]$) from the data of Fig. 1 on Ag(110) is shown directly as function of temperature in Fig. 2. There is a gradual decrease in selectivity with increasing temperature on Ag(110), again in agreement with the trend seen on most high-surface-area catalysts [10,12,13]. The absolute value of the selectivity (~55%) on Ag(110) falls within the range seen for unpromoted, high-surface-area Ag catalysts as can be seen by comparison in Fig. 2.

In Fig. 3 we show the effect of O_2 pressure upon the steady-state rate of EtO production at 490 K and 30 torr ethylene. Note the excellent agreement with the results for a high-surface-area, alumina-supported Ag catalyst. At low P_{O_2}, the rate is close to first order in P_{O_2}. For $P_{O_2} \gtrsim 8 \times P_{Et}$, the order in P_{O_2} approaches zero.

In a related paper [1], we have further demonstrated that the effects of ethylene and O_2 pressure upon the rates of EtO and CO_2 production and upon the selectivity are virtually identical on Ag(110) and relatively high-surface-area Ag catalysts.

In Table I, we make a direct comparison between the absolute specific rates (per Ag surface atom) measured here on a clean Ag(110) surface and those measured previously on a variety of unpromoted high-surface-area Ag catalysts. The specific Ag surface areas (m^2 of Ag per gram) and the methods of determination are also listed. For the high-surface-area catalysts, we have assumed 10^{15} Ag surface atoms (sites) per cm^2 of silver area. Unfortunately the conditions of temperature and pressure vary somewhat in Table I, but conditions which gave higher rates (i.e. higher T,P) than those used for Ag(110) were chosen where available. The trend in Table I is, nevertheless, quite clear: the specific activity of Ag(110) is about a factor of 200 higher than that of the relatively high-surface-area catalysts which, among themselves, show considerable variation. We point out that the last entry in Table I(*) for silica-supported Ag uses a specific Ag area determined in an unreliable fashion (BET surface area). We provide this entry only because it was the catalyst used for the data in Figs. 1-2. It falls, however, almost at the average of activity found for high-surface-area Ag catalysts. We found from the literature that the BET surface area of supported Ag catalysts was often quite close to the Ag surface area [7,9,11].

IV. DISCUSSION

Our data indicate a much higher catalytic activity for epoxidation per surface silver atom for the clean Ag(110) surface than for unpromoted, high-surface-area Ag catalysts. It is not clear what the densities of low-index planes on the surface of a high-surface-area Ag catalyst are, particularly under reaction conditions where rearrangement can occur [5,14]. However, one might guess a high portion of (111) or (100) planes [24], relative to the rather open (110) plane. Ag(110) appears to be much more active catalytically than whatever combination of surfaces exist on a high-surface-area catalyst. We have planned experiments to test the specific activity of Ag(111) and/or Ag(100) in this reaction. A strong variation in activity among the crystal planes is certainly consistent with the well-known structural sensitivity of Ag catalysts in this reaction [4-8]. For small Ag particles, the specific activity decreases with particle size [6-8]. A minimum in specific activity is reached at silver crystallite sizes of 500-700 Å, above which the specific activity grows [7]. Selectivity increases with particle size for small particles [6-8] but decreases for very large particles [7]. This behavior is quite complex, but is most probably related to changes in the density of certain more active planes with particle size. The catalytic activity of a plane has been shown for some reactions to be determined by the types of bonding sites it exhibits for adsorption [25]. Our observation of a high catalytic activity for the rather open (coordinatively less saturated) Ag(110) plane is consistent with the trend for small Ag particles of increasing activity with decreasing particle size. Smaller particles should exhibit a higher density of coordinatively unsatisfied surface atoms. Interestingly, the Ag(110) plane has a much higher activity for dissociative oxygen adsorption than other low-index planes of Ag, particularly Ag(111) [22,26]. In light of our recent results which highlight the critical role played by O_a in the reaction kinetics [1], we suggest that this is related to the high activity of Ag(110) for ethylene epoxidation. At constant temperature and ethylene pressure, the rate of EtO production on Ag(110) was first-order in the coverage of atomically-adsorbed oxygen [1].

A very early attempt was made to compare the relative activities of Ag single crystals cut along various planes in this reaction [15]. No more than a factor of three variation was found among the five surfaces compared, with Ag(111) giving the lowest and polycrystalline Ag giving the highest specific activity for EtO production. (Other surfaces compared were 8° from [211], 3° from [110], and 9° from [110].) These experiments were, unfortunately, unaccompanied by any surface analysis so that the actual orientation, order, defect density, and cleanliness of the surface layer were not verified. While the specific activities of these bulk samples ($TON_{EtO} \simeq 0.15$ molecules $site^{-1}s^{-1}$ at 483 K, $P_{O_2} = 110$ torr, $P_{Et} = 55$ torr) was considerably larger than that reported in Table I for high-surface-area catalysts, they were still a factor of about ten below our present results for Ag(110). Results for initially oriented Ag films [14] indicate a low specific activity, consistent with the data in Table I for high-surface-area catalysts. These films were shown to reorient under reaction conditions [14]. One might postulate that highly dispersed or supported Ag samples reorient to some relatively inert surface configuration under reaction conditions due to the large exothermicity of the reaction (24.7 and 320 kcal per mole Et for EtO and CO_2 production, respectively). Bulk Ag samples, on the other hand would be more inert to such energy-driven reorientation due to the more efficient energy dissipation in a bulk metal, and might therefore be capable of maintaining the active orientation at the surface.

We have shown that the effects of temperature, P_{O_2} and P_{Et} upon the reaction rates are virtually identical on Ag(110) and high-surface-area, supported catalysts, yet the specific activity is some 100-fold higher for Ag(110). It is hard to rationalize these two observations without assuming that it is a small percentage of Ag(110) planes (or related sites) on a high-surface-area catalyst which gives rise to most of its catalytic activity.

In light of our present results, one cannot help but wonder if perhaps a high-surface-area Ag catalyst might someday be synthesized and stabilized which predominates in (110)-like sites.

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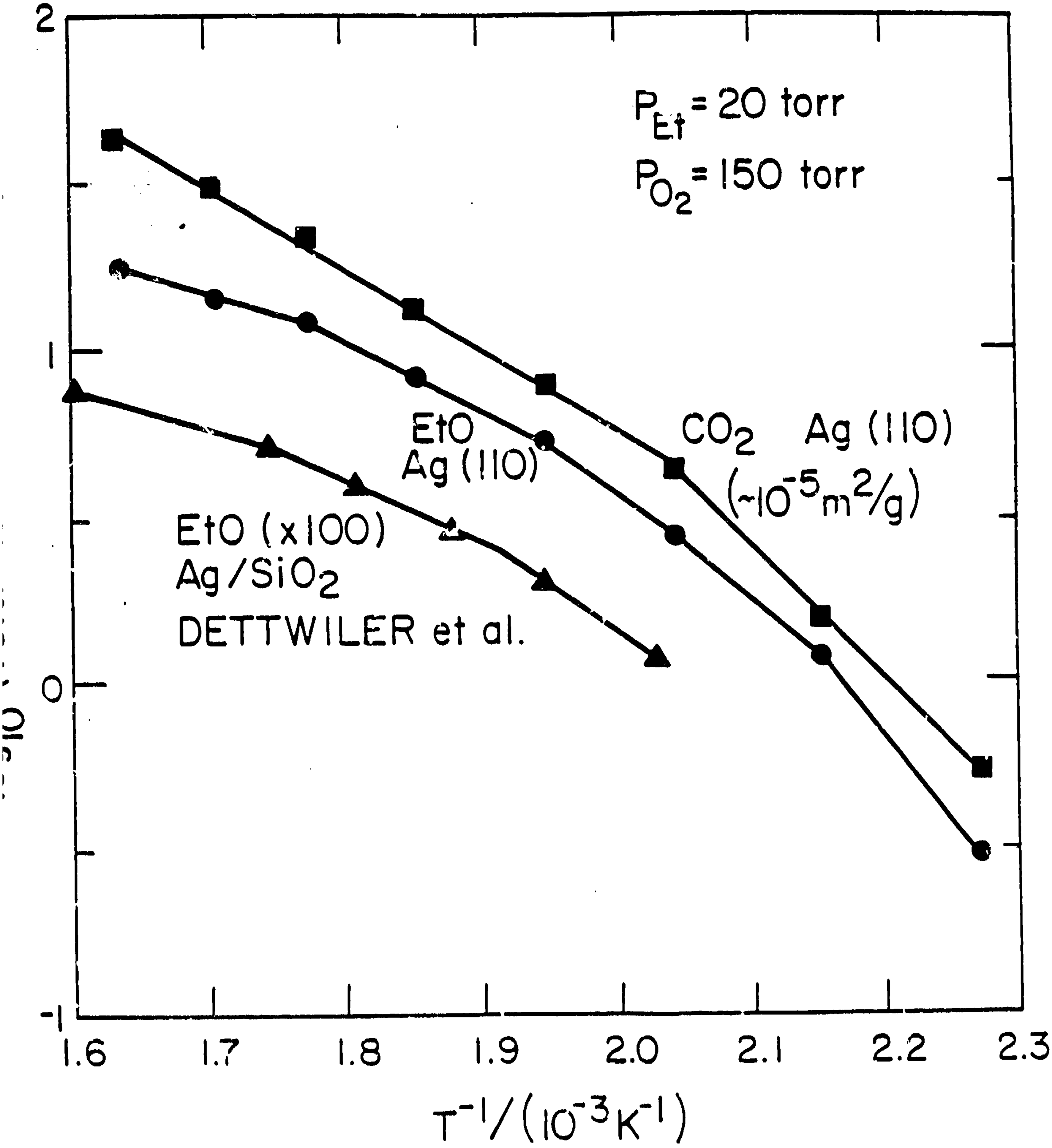
LIST OF FIGURES

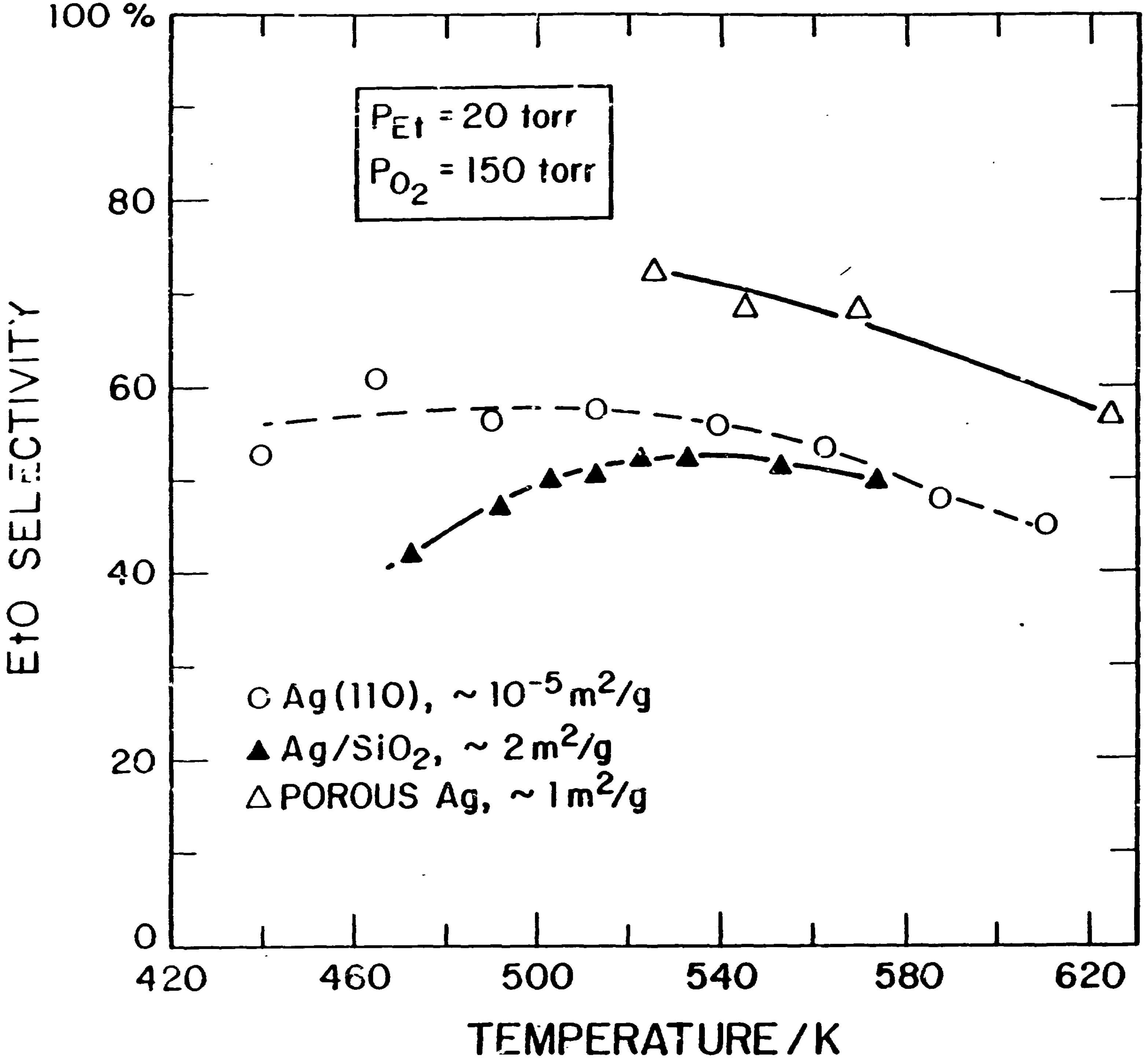
Figure 1. Steady-state rates of EtO and CO_2 production versus temperature in Arrhenius form at P_{Et} = 20 torr and P_{O_2} = 150 torr over Ag(110). Shown also is the rate of EtO production (X100) over a $2m^2/g$ Ag catalyst supported on pumice (mostly SiO_2) taken from [12].

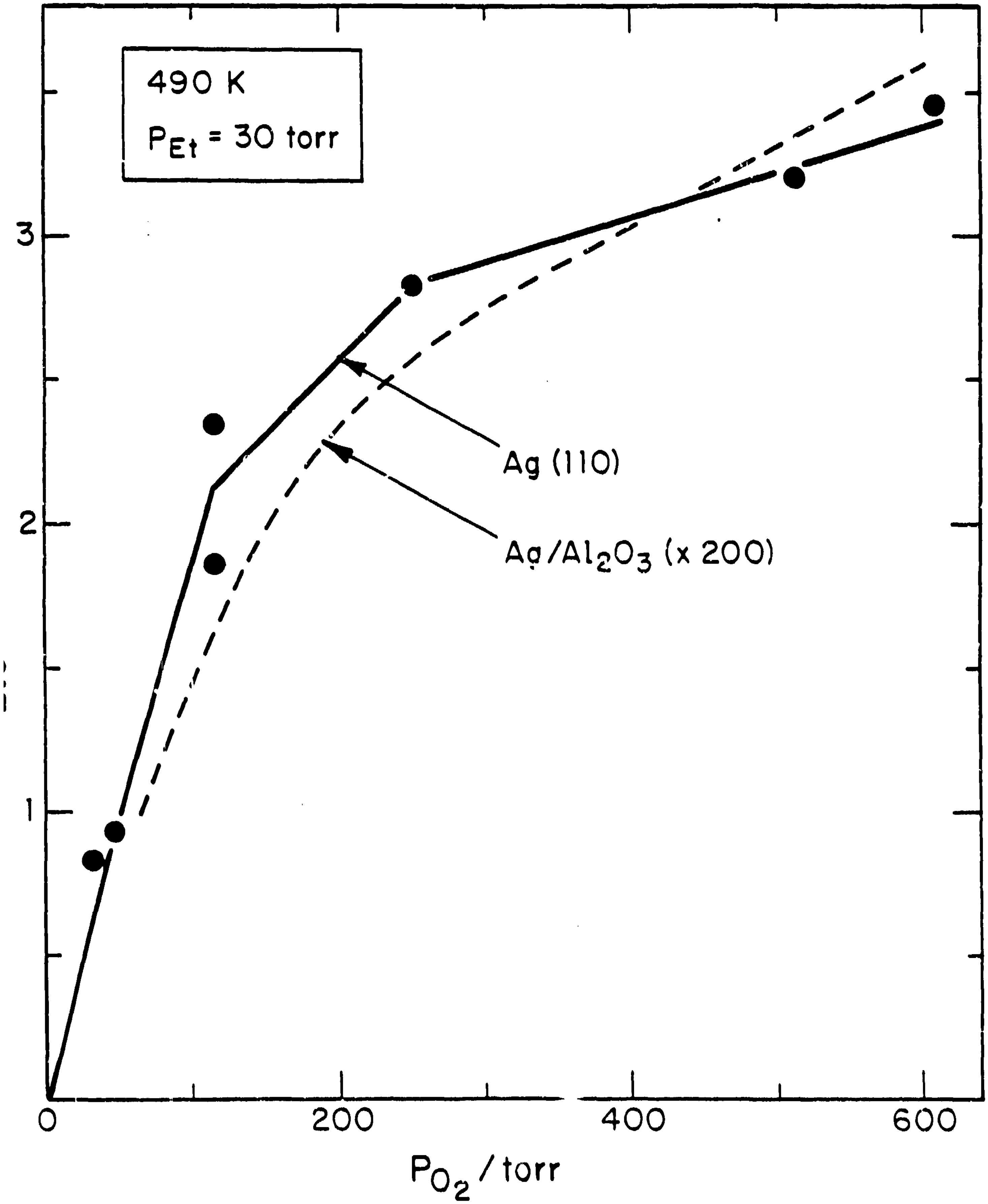
Figure 2. The Ag(110) data of Fig. 1 replotted to directly show the effect of temperature upon selectivity. Shown for comparison are data under very similar conditions for silica-supported Ag($\sim 2m^2/g$) [12] and a porous Ag film ($\sim 1m^2/g$) [10].

Figure 3. Steady-state rate of EtO production versus O_2 pressure at 490 K and 30 torr ethylene over Ag(110) and silver-impregnated α-Al_2O_3 (X200) of ~ 0.2 m^2 of Ag per gram [11].

Table I. A comparison of specific reaction rates (TON) for ethylene epoxidation per Ag surface atom (site) at similar reaction conditions (as listed) for Ag(110) and a variety of relatively high-surface-area, unpromoted, supported and unsupported Ag catalysts extracted from the references listed. The specific Ag surface areas and their method of determination are also listed: O_2-TDS = O_2 thermal desorption spectroscopy; O_2-Ads = O_2 chemisorption; TEM = electron microscopy; BET = BET surface area.


P_{Et} = 20 torr
P_{O_2} = 150 torr
EtO
Ag (110)
CO_2 Ag (110)
($\sim 10^{-5} m^2/g$)
EtO (x100)
Ag/SiO_2
DETTWILER et al.
2
1
0
-1
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
$T^{-1}/(10^{-3}K^{-1})$


100 %
80
60
40
20
0
420
460
500
540
580
620
TEMPERATURE / K
EtO SELECTIVITY
P_{Et} = 20 torr
P_{O_2} = 150 torr
○ Ag(110), ~ 10^{-5} m^2/g
▲ Ag/SiO_2, ~ 2 m^2/g
△ POROUS Ag, ~ 1 m^2/g


490 K
P_{Et} = 30 torr
Ag (110)
Ag/Al_2O_3 (x 200)
3
2
1
0
200
400
600
P_{O_2} / torr

SPECIFIC ACTIVITIES FOR ETHYLENE EPOXIDATION

MATERIAL	SPECIFIC AREA M^2_{Ag}/g	TON-EtO $site^{-1} \cdot s^{-1}$	TEMP. K	P_{O_2} torr	P_{Et} torr	AREA METHOD	REF.
Ag(110)	$\sim 10^{-5}$	2	490	150	20	geometric $+O_2$-TDS	present
Ag/SiO_2	40	10^{-1}	473	96	164	O_2-Ads. + TEM	6
$Ag/\alpha Al_2O_3$	0.5	10^{-2}	513	170	342	O_2-Ads.	7
Ag/SiO_2	40	10^{-3}	493	200	200	O_2-Ads. + TEM	8
~Raney Ag	0.5	10^{-1}	547	150	18	BET	9
Porous Ag Film	1	$10^{-1.5}$	523	76	8	BET	10
$Ag/\alpha Al_2O_3$	0.5	10^{-2}	493	200	20	TEM	11
Ag/SiO_2	2	10^{-2}	523	150	20	BET *	12

Table 1