JOURNAL OF CATALYSIS 23, 379–387 (1971)

Catalytic Oxygen Transfer between Ethylene and Ethylene Oxide

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Received April 20, 1971

The transfer of oxygen between ethylene and ethylene oxide has been studied at surfaces of Ag, Au, $(VO_2)_x$, and bismuth molybdate. The study was carried out by following the rate of redistribution of isotopic carbon between ethylene and ethylene oxide. The conditions employed in the experiments were: temperature 22–305°C, partial pressure ratios of ethylene oxide to ethylene 0.1–50, contact time 1–10 sec. Silver was supported on high- and low-area Al_2O_3 zeolite and complexed with poly(4-vinylpyridine). Au was supported on Al_2O_3 and MgO. The dependence of the rate of isotopic redistribution upon the ratio of ethylene oxide to ethylene was taken as an indication of the process of reactive and competitive chemisorptions of ethylene and ethylene oxide. Information on the nature of the adsorption, in terms of number of surface centers per adsorbate molecule, was derived. From this point of view, the catalysts tested may be divided into two groups. In one group, single-center adsorption of ethylene predominated, while in the second the adsorption of ethylene included two surface centers per molecule. Thus, on the first group, ethylene fragmentation should not be favored. These catalysts, therefore, should prove more selective to ethylene oxide in the net reaction of ethylene oxidation with molecular O_2. These predictions are fully confirmed by direct experimentation.

The majority of the studies on the catalytic oxidation of ethylene (ET) with molecular oxygen have emphasized the role of different forms of adsorbed oxygen in the formation of the products: ethylene (*1*) oxide (ETO), carbon dioxide, and water. The studies have supplied strong evidence for the presence at catalytic surfaces, particularly those of Ag, of adsorbed oxygen in the molecular and atomic states and given support to the suggestion that the formation of ETO in high yields (60–70%) and reaction conversions (>40%) is dependent upon the presence of the molecularly adsorbed form. According to this view, the problem of reaction selectivity is one of oxygen adsorption.

Except for some early suggestions (*2, 3*) similar attention has not been paid to the interaction between catalyst and ET. The possibility that different forms of the former may variously contribute to the oxidation product cannot be dismissed and should be considered. It is conceivable that the selectivity of the oxidation reaction results from factors dependent upon the adsorption of O_2 and ET.

To further investigate this question, the present study was undertaken. Specifically, the work was aimed at finding out whether and, if so, the extent to which different adsorption modes of ET contribute to the formation of ETO in the catalytic oxidation of the former. To carry out this task and clearly separate any influence of the adsorption of molecular oxygen, it was decided to carry out the oxidation of ET by means of ETO itself. This molecule constitutes a special oxygen donor since it is related to the acceptor by a unique re-

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lationship, viz., that of simple reversibility. In fact, in the oxidation of ET by ETO, and in the absence of side reactions there is no change in the total number of molecules, since every oxidation to ETO is accompanied by a reduction to ET. Consequently, the use of ETO as oxygen donor permits the study of the rate of oxidation of ET under conditions approaching thermodynamic equilibrium. In this fashion it is possible to investigate the role of the concentration of adsorbed intermediates upon the rate of interaction of ET with the reactive catalyst surface. Because of these theoretical possibilities, in addition to the experimental advantages of studying the reaction rate of a system at chemical equilibrium, the method seemed of sufficient interest to warrant a detailed investigation.

This was carried out by finding the experimental conditions under which the rate of catalytic redistribution of ^{14}C between ET and ETO, viz.:

$$^*C_2H_4(g) + C_2H_4O(g) \rightarrow C_2H_4(g) + {}^*C_2H_4O(g) \quad (1)$$

could be conveniently studied without interference from polymerization of ET and/or isomerization and decomposition of ETO. If it is assumed that adsorbed oxygen, O(s), is the intermediate during the course of reaction (1), the latter may be visualized as the sequence of two adsorption steps, viz.:

$$^*C_2H_4(g) + O(s) \rightarrow {}^*C_2H_4O(g), \quad (1a)$$

$$C_2H_4O(g) \rightarrow C_2H_4(g) + O(s). \quad (1b)$$

Since the reaction step (1b) is the reverse of reaction step (1a), and since reaction (1) represents a chemical equilibrium, the rates of reaction steps (1a) and (1b) are similar to that of reaction (1). Thus, measurements on the rate of reaction (1) give directly the rate of reaction steps (1a) and (1b). Neglecting kinetic isotopic effects, reaction step (1a) corresponds to the reactive adsorption of ET on the oxygenated catalyst surface producing ETO. Since this may be an important step of the net oxidation, it is clear that the study of the rate of reaction (1) represents a kinetic tool which may be advantageously employed to characterize the thermodynamic and kinetic nature of the adsorption of ET and to define its possible role in the net oxidation to ETO. Since the virtual equilibrium oxygen pressure corresponding to reaction step (1b) is several orders of magnitude smaller than the partial pressure of molecular oxygen generally employed (~1 atm) in the net oxidation reaction, it is likely that complete definition of the latter cannot be achieved without consideration of the adsorption step of molecular oxygen.

We have studied the rate of reaction (1) on four Ag catalysts, whose characteristics for the oxidation of ET by O_2 were independently determined by measurements of the rate of the net oxidation reaction. We also investigated the catalytic activity for reaction (1) of suported Au preparations, a Ag–polymer complex, SiO_2-supported bismuth molybdate, and unsupported (VO_2).

EXPERIMENTAL

Materials

High-purity compressed gases were used throughout. Ethylene oxide and ethylene dichloride (reagent grade) were commercial products, and were used without further purification. One millicurie, ^{14}C-labeled C_2H_4 was mixed with nonradioactive ET (>99.5%) and stored in a cylinder under pressure. The carrier gas was high-purity Ar (>99.995%). Five Ag catalysts were studied. Ag-1 was prepared by reacting at room temperature solutions of $AgNO_3$ and Na_2CO_3. The dried precipitate of Ag_2CO_3 was added to an excess of lactic acid (85% H_2O solution) at 90°C under vigorous stirring, the molar ratio $AgCO_3$/lactic acid was 1:2.2. H_2O_2 (30%) was then added. To the clear solution of Ag lactate, Ca and Ba lactates were added. Support impregnation was carried out at 90°C. The catalyst, dried overnight under a stream of air, was calcined at 315°C for 5 hr in air. Ag-2 was prepared by dissolving Ag oxide in lactic acid (85% H_2O solution) at 100°C. H_2O_2 and Ba lactate were subsequently added. Support impregnation took place at 100°C. The dried catalyst was heated at 400°C for 12 hr in a stream of H_2. Ag-3 was prepared by following the same procedure used for Ag-1, but only Ba lactate was added. Ag-4 was prepared by treating Y zeolite with $AgNO_3$ solution (20% H_2O). The impregnated zeolite was dried at 80°C for 12 hr in air and for 6 hr in a stream of H_2. One thousand grams of the Ag containing zeolite were then treated with 100 g of $NaNO_3$ in 4000 cm^3 of H_2O. After repeated washing with distilled H_2O, the zeolite was dried at 80°C overnight and at 250°C for 5 hrs in an air stream. Ag-5 was prepared by adding a solution of $AgNO_3$ in $CH_3OH + H_2O$ to a solution of poly(4-vinylpyridine) in CH_3OH. The precipitate was filtered, dried under vacuum, and used without further purification. Chemical composition of the catalysts was obtained by the Volhard method for Ag analysis. Ag surface areas were measured by O_2 adsorption, X-ray diffraction (in the range 50–800 Å) and electron microscopy. A summary of the characteristics of Ag catalysts is presented in Table 1.

Two supported Au catalysts were tested. They were prepared by addition of a solution of $HAuCl_4 \cdot 3H_2O$ to a weighted amount of reagent grade MgO (18 m^2/g surface area). The slurry was air dried and heat treated at 350°C for 2 hr at 0.1 Torr (decomposition) or reduced at 100°C with a 3% solution of oxalic acid and subsequently dried and heat treated in a similar fashion (reduction). More details on the preparation and characterization of the Au catalysts may be found elsewhere (*4*). The characteristics of Au catalysts are summarized in Table 2.

TABLE 2
CHARACTERISTICS OF MgO SUPPORTED Au CATALYSTS

Catalyst	Preparation method	Au Wt %	Au Surface area[a] (m^2/g)
Au-1	Decomposition	0.7	0.0165
Au-2	Reduction	2.0	1.24

[a] X-Ray diffraction assuming spherical particles.

The bismuth molybdate catalyst (Bi–Mo–O) was prepared by slowly adding a solution of $Bi(NO_3)_3 \cdot 5H_2O$ in dilute HNO_3 to an ammonia solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. After stirring, the required amount of collodial SiO_2 catalyst (particle size 130–140 Å) was added to make a 60% by weight of supported catalyst. After drying, the catalyst was pelletized (6 mm diam, 4 mm height) and calcined in air up to 500°C. The surface area was 100 m^2/g and the composition 19.0% Bi_2O_3, 17.9% MoO_3, and 63.1% SiO_2. (VO_2) was a commercial preparation of 99% purity. Its surface area was 16 m^2/g.

All catalysts, except $(VO_2)_x$, were ground and seived; the fraction between 30 to 45 mesh was used. *In situ* pretreatment was as follows: Ag–Au catalysts were treated in the reactor for about 6 hr at reaction conditions. $(VO_2)_x$ was initially treated overnight in a stream of Ar + ET. After this treatment, it was found to be too ac-

TABLE 1
CHARACTERISTICS OF Ag CATALYSTS

	Support			Composition		Ag	
Catalyst	Type	Porosity (cm^3/g)	Ave pore diam (Å)	Ag (wt %)	Additions (molar ratio)	Surface Area (m^2/g)	Crystallite size (Å)
Ag-1	α-Al_2O_3	0.31	5000	15.3	Ag:Ba:Ca = 1400:7:0.25	11.3	500
Ag-2	α-Al_2O_3	0.23	200 000	15	Ag:Ba = 1400:7	1.1–1.2	3000–5000
Ag-3	γ-Al_2O_3	0.80	250	21.3	Ag:Ba = 1400:7	50	100
Ag-4	Zeolite Y	1.30	~10	22.0	Ag:Na = 2.24	150	30–50
Ag-5	Ag-poly (4-vinylpyridine) complex			23.8	—	—	30–40

tive and to decompose ETO extensively at room temperature. ETO was then added to the pretreatment mixture. The activity was reduced and experiments on reaction (1) could be performed without interference from side reactions. The Bi-Mo-O catalyst, when pretreated overnight in a stream of ET–ETO–Ar, showed a very high activity in the decomposition of ETO even at —25°C. By employing ETO only in the pretreatment, and continuing the pretreatment for 72 hr it was possible to observe the rate of reaction (1) without excessive ETO decomposition ($<2\%$). During this treatment the color of the catalyst changed from yellow to greenish-blue, probably indicating reduction to $\mathrm{Mo^{V}}$ and $\mathrm{Mo^{IV}}$.

Equipment

The rate of reaction (1) was studied in a flow system at atmospheric pressure. Metered streams of Ar, *ET, and ET were dried over $MgClO_4$ and led to the reactor. Additional streams of Ar flowed into a C_2H_4O saturator maintained at low temperature (—70 to 0°C) with a slush bath of Dry Ice and isopropyl alcohol and, in some experiments, into a saturator containing $C_2H_4Cl_2$, maintained at —20°C. The glass reactor had a by-pass for analyzing the feed mixture. Analysis was performed by gas chromatography (gc). The gc column employed was filled with Porapak Q and permitted easy separation of ET, ETO, and acetaldehyde at a temperature of 150–180°C. The fractions eluting from the chromatograph (except for acetaldehyde) were collected in a solution of PPO in toluene for liquid scintillation analysis. CO_2 was analyzed gravimetrically as $BaCO_3$. Measurements on the oxidation selectivity ETO were carried out in a flow reactor with a feed of composition (vol %): ET 5,O_2 5,CO_2 6.5, the remaining being N_2. The space velocity employed was 66.6 $\mathrm{cm^3}$ STP/min·g(Ag)·5 ppm of $C_2H_4Cl_2$ were added to the feed except for Au and $(VO_2)_x$.

Procedure

Before each measurement of composition and radioactivity on the exit stream of the reactor, a sample of the inlet stream was collected and analyzed. The radioactive count of the ETO fraction in the inlet stream was used as the background count. Tests were also performed by flowing the reaction stream through the empty reactor at temperatures up to 300°C. No significant amount of conversion was observed. Counting cycles from 10 to 150 min were used, and the corresponding statistical error was 2% for ETO and 1% for ET. The presence or absence of CO_2 in the effluent gas was determined by collecting the effluent in a solution of $Ba(OH)_2$ and titrating it. The operating conditions chosen for the study of every catalyst were such that in every case $<3\%$ of CO_2 was produced, and no detectable amounts of ETO were isomerized to acetaldehyde. The experimental error in the values of the parameters k and m (see below) were estimated at 30 and 5%, respectively.

Experimental Results

The rate of reaction (1) (or reaction steps (1a) is given by:

$$-(1/W)(dp_{*\mathrm{ET}}/dt) = k_c p_{*\mathrm{ET}} - k'_c p_{*\mathrm{ETO}}, \qquad (2)$$

where k_c, k'_c are dependent on the ratio $p_{\mathrm{ETO}}/p_{\mathrm{ET}} = \beta$, and W is the catalyst weight. Introducing the equilibrium condition into Eq. (2), rearranging, integrating, and solving for k_c, one obtains for a flow reactor:

$$k_c = \frac{1}{W}\frac{\dot{V}}{RT}\frac{1}{1+(1/\beta)}\ln\frac{1}{1-\alpha}, \qquad (3)$$

where $\dot{V}$, R, T, and α are the total volumetric flow rate at room temperature T, the gas constant and $\alpha = p_{*\mathrm{ETO}}/(p_{*\mathrm{ETO}})_e$, where the suffix e refers to equilibrium conditions.

On Ag-1 and Ag-2 it was found that the convenient temperature range for the study of the rate of reaction (1) was 174–204°C. At 174°C no isomerization of ETO to acetaldehyde was detected, while at 204°C there was extensive ($\leq 50\%$) decomposition to CO_2. The addition of 4–5 ppm of $C_2H_4Cl_2$ to the feed stream reduced the amount of CO_2 to $<3\%$. The organic halide however, did not have any noticeable

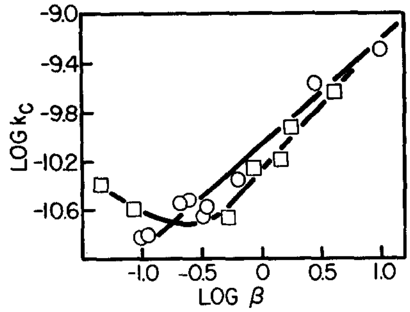

FIG. 1. Values of k_c vs β for reaction (1) catalyzed by Ag-1, □; Ag-2, ○; 204°C.

influence on the isomerization of acetaldehyde. At temperatures <174°C the rate of reaction (1) on Ag-1 was too slow for convenient study. Values of k_c, calculated by means of Eq. (3), are reported as a function of β for Ag-1 and Ag-2 at 204°C in Fig. 1.

The temperature range for a convenient study of the rate of reaction (1) on Ag-3, Ag-4, and Ag-5 was drastically different. To avoid decomposition to CO_2, considerably lower reaction temperatures were needed. In Fig. 2, we report the results on Ag-3, Ag-4, and Ag-5 in the temperature range 38–77°C. At 100°C, in the presence of Ag-3, 90% of ETO was decomposed to CO_2 even with the addition of 5–10 ppm of $C_2H_4Cl_2$ to the feed mixture. The experimental results on the supported Au catalysts are shown in Figs. 3 and 4. Figure 3 summarizes the values of k_c as a function of β, recorded for Au-1 at 270 and 290°C, while Fig. 4 those on Au-2. No $C_2H_4Cl_2$ was employed in these runs. In Fig. 5 we have collected the experimental results on $(VO_2)_x$ at 177°C, and on Bi–Mo–O at 22°C.

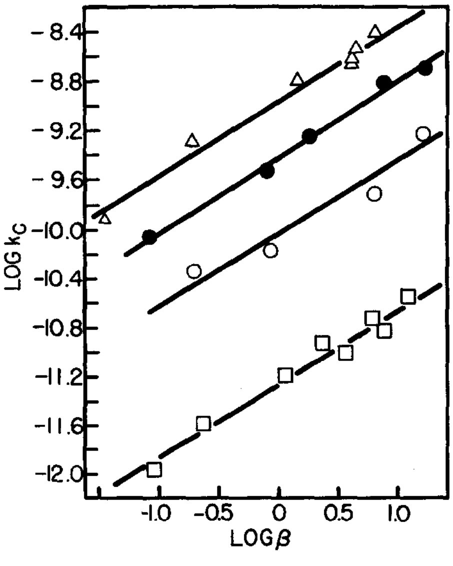

FIG. 2. Values of k_c vs β for reaction (1) catalyzed by Ag-3, □ (38°C); Ag-4, ○ (57°C), ● (77°C); Ag-5, △ (65°C).

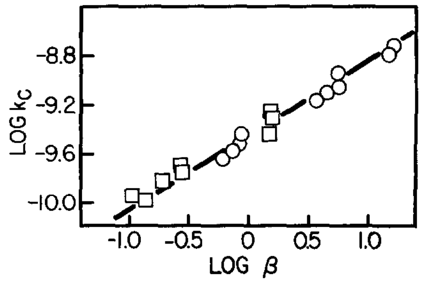

FIG. 3. Values of k_c vs β for reaction (1) catalyzed by Au-1, □, 270°C; ○, 290°C.

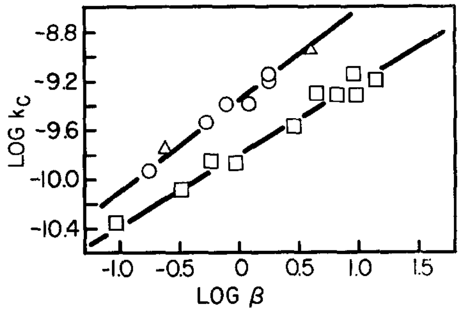

FIG. 4. Values of k_c vs β for reaction (1) catalyzed by Au-2, □, 177°C; ○, 280°C; △, 305°C.

The experimental results in Figs. 2–5 may be expressed by the relation

$$k_c = k\beta^{\pm m}, \tag{4}$$

where k and m are constants, whose values are collected in Tables 3–5.

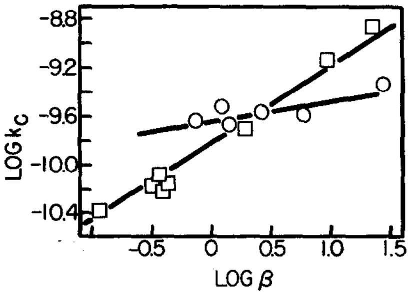

FIG. 5. Values of k_c vs β for reaction (1) catalyzed by $(VO_2)_x$, □, 177°C and Bi–Mo–O, ○, 22°C.

TABLE 3
VALUES OF m AND k (EQ. (4)) FOR REACTION (1) CATALYZED BY SUPPORTED Ag

Catalyst	Temp (°C)	m	$k \times 10^{10}$ $\left[\frac{\text{mole}}{\text{g(cat) sec atm}}\right]$
Ag-1	174	−1, 1.0	2.1
	204	−0.17, 1.25	4.0[a]
Ag-2	204	0.90	8.3
Ag-3	38	0.60	0.54
	48	0.58	0.23
Ag-4	57	0.58	1.0
	77	0.59	37
Ag-5	65	0.59	110

[a] Five ppm $C_2H_4Cl_2$ added.

TABLE 4
VALUES OF m AND k (EQ. (4)) FOR REACTION (1) CATALYZED BY SUPPORTED Au

Catalyst	Temp (°C)	m	$k \times 10^{9}$ $\left[\frac{\text{mole}}{\text{g(cat) sec atm}}\right]$
Au-1	270–290	0.62	3.6
Au-2	177	0.59	1.6
	280–305	0.76	4.5

TABLE 5
VALUES OF m AND k (EQ. (4)) FOR REACTION (1) CATALYZED BY $(VO_2)_x$ AND Mo–Bi–O

Catalyst	Temp (°C)	m	$k \times 10^{9}$ $\left[\frac{\text{mole}}{\text{g(cat) sec atm}}\right]$
$(VO_2)_x$	177	0.66	1.4
Bi–Mo–O	22	0.16	1.7

DISCUSSION

The significant conclusions which may be drawn from the results of the previous section are:

1. On all the catalysts studied the rate of reaction (1) was quantitatively followed without serious interference from side reactions. In some instances, to avoid isomerization and decomposition of ETO, a limited range of the experimental variables was available and greatly different temperature regions were employed.
2. For all the catalysts tested, the rate of reaction (1) increased with increasing β. For catalyst Ag-1 there was a change in the sign of this relation at the lower values of β.
3. The values of the exponent m in Eq. (4) were $\sim$1 for Ag-1 and Ag-2 and $\sim$0.6 for Ag-3, Ag-4, and Ag-5. For Au catalysts and $(VO_2)_x$ $0.5 < m < 1$ while on Bi–Mo–O the rate of reaction (1) was found to be almost independent of β.

Item one indicates that despite the large differences in the physical and chemical characteristics of the substances employed and of their surfaces, experimental conditions exist under which the adsorption–desorption of ET and ETO are the preponderant molecular processes taking place. The wide variation in temperature necessary to observe conveniently the rate of reaction (1) reflects the different reactivity of the substances employed. Item 2 is a consequence of the mixed adsorptions of ET and ETO. Since measurements were carried out by observing the formation of ETO containing ^{14}C from radioactive ET the rate of the process should be dependent upon the extent of the surface available for adsorption of ET in the presence of ETO. Thus, the rate of exchange reaction (1) [or reaction step (1a)] is governed by the concentration of surface sites available for ET adsorption. Conceivably, these are sites containing oxygen in the form of some kind of adsorbed ETO. Thus, if adsorption of ET and ETO requires one surface site per molecule adsorbed (single-site adsorption), the concentration of surface sites available will be $\propto p_{ETO}/p_{ET}$ while on surfaces requiring one pair of adjacent sites per adsorbed molecule (two site adsorption), the concentration of single surface sites available for ET adsorption will be $\propto (p_{ETO}/p_{ET})^{1/2}$. As a result, on surfaces whose preponderant ET–ETO adsorption is the single-site type, the rate of the exchange reaction (1) is expected to be $\propto p_{ETO}/p_{ET}$ while on those requiring two-site adsorption the rate should be $\propto (p_{ETO}/p_{ET})^{1/2}$. A rather intuitive interpretation of these types of adsorptions involves the interaction with π-electrons of the double bond for the single-site process (nondissociative) and disappearance of the double bond for the two-site process (dissociative adsorption).

This simple interpretation of the adsorption of ET may be generalized. If two neighboring sites are necessary (ions and electrons, atoms and molecules) fragmentation of the adsorbate may follow. Conceivably only one-site adsorption played a dominant role in the oxidation experiments reported in the previous section, since any fragmentation of ET at the catalyst surface involves a more complex and, therefore, less likely route for the transfer of oxygen and lead to products (CO_2) which were either present in small amounts or absent from the gas phase. As a consequence of this, the rate of reaction (1) should be $\propto \beta$ at those surfaces at which one-site adsorption predominates, while $\propto \beta^{1/2}$ whenever two-site adsorption is the major type of adsorption. Cases of mixed types of adsorption are shown by powers intermediate between 0.5 and 1, while adsorptions with increasing amounts of fragmentation may be represented by an exponent <0.5. Experimentally it was found that for Ag-1 and Ag-2, the rate of reaction (1) was $\propto \beta$ while for Ag-3, Ag-4, and Ag-5 $\propto \beta^{1/2}$ (Item 3). It is tempting to suggest that under the experimental conditions employed, ET adsorption took place essentially by one site per molecule on the surfaces of Ag-1 and Ag-2, while a two-site adsorption was the predominant manner with which ET was adsorbed on Ag-3, Ag-4, Ag-5, and Au-1. Au-2 and $(VO_2)_x$ represented intermediate situations, while on Bi–Mo–O ET adsorption was tantamount to extensive fragmentation.

This conclusion on the fundamental characteristics of ET and ETO adsorption may be put to an intesting test. At surfaces where one-site adsorption predominates and C=C bond fission is low, it is reasonable to expect a high probability of ETO desorption during the oxidation of ET with O_2, conversely for a surface where two-site adsorption is the main mode. Consequently it should be possible to predict the selectivity characteristics of catalyst surfaces from the value of m as determined from the rate of the isotopic exchange reaction (1). From the results reported in Table 5, this criterium predicts that catalysts Ag-1 and Ag-2 should have high selectivity, while catalysts Ag-3 and Ag-4 low selectivity towards the formation of ETO from ET and O_2. To check this prediction, the selectivity of the catalysts was experimentally measured. The results are reported in Table 6.

The experiments reported in Table 7 fulfilled in a striking fashion the predicted selectivity sequence among the four Ag catalysts. On the strength of this finding, it became of interest to investigate the extent to which the criterium may be valid for substances other than Ag. To this purpose,

TABLE 6

SELECTIVITY TO ETO IN THE OXIDATION OF ET WITH O_2 OVER SUPPORTED Ag CATALYSTS

Catalyst	Temp (°C)	Reaction[a] conversion (%)	Selectivity to ETO[b] (%)
Ag-1	193	20	72
Ag-2	216	20	72
Ag-3	140	20	0
Ag-4	140	20	0

[a] Moles C_2H_4 reacted/moles C_2H_4 fed × 100.

[b] Moles C_2H_4O formed/moles C_2H_4 reacted × 100.

TABLE 7

SELECTIVITY TO ETO IN THE OXIDATION OF ET WITH O_2 OVER SUPPORTED Au AND $(VO_2)_x$

Catalyst	Temp (°C)	Reaction conversion (%)	Selectivity ETO (%)
Au-2	200	0	0
	250	0	0
	280	12.6	0
	304	26.5	0
$(VO_2)_x$	230	4.7	0
	260	13.0	0

two additional catalysts were tested in the net oxidation of ET. The results are collected in Table 7. The results of Table 7 further support the relation between the values of the exponent m and catalyst selectivity and give added confidence that the former is not restricted to Ag catalysts, but may be valid for chemically different surfaces. On the strength of this finding, it is safe to conclude that selectivity characteristics of Ag catalysts are not dependent solely on the nature of the adsorption of O_2 but that an important contribution is derived from ET adsorption. Thus, this conclusion supports the earlier suggestion, which was derived from studies on the net oxidation reaction (*2*).

On Ag-1 at the lower end of the values of β, the rate of reaction (1) decreased with increasing β. In terms of the scheme of competitive adsorption of ET and ETO mixtures set forth above, the effect is the result of an increased surface monopoly by ET as p_{ET} increases. Intuitively, this behavior indicates that the rate of formation of ETO from ET and O_2 should pass through a maximum with increasing p_{ET}. This has been observed (*5*).

In the last column of Tables 3 to 5 the values of the reaction rate constants, k, calculated by means of Eq. (4) are reported. From the values of k, it is clear that reaction (1) has a very low probability of occurrence. However, differences in rate constants by about three orders of magnitude among the catalysts tested were found. To perform a more accurate comparison the rate constant per unit metal (Ag, Au) or total $(VO_2)_x$ surface area k' were computed and are reported in Table 8.

Inspection of Table 8 shows that the values of k' vary between seven orders of magnitude. Disregarding differences in temperature, the activity sequence is as follows: Au-1 > Au-2 > Ag-2 > $(VO_2)_x$, Ag-4 > Ag-1 > Ag-3. These results do not support an inverse relationship between activity and selectivity, as it has often been claimed to exist. On the basis of our results, it sems more likely that the activity is related to specific surface features—its chemistry and structure—while the selectivity is dependent upon the nature of the adsorption of oxygen and ethylene. Of course the latter is not independent of the former, but it tends to control more directly the kinetic path of the reaction.

TABLE 8
RATE CONSTANT PER UNIT REACTIVE AREA k', FOR REACTION (1)

Catalyst	Temp (°C)	k' $\left[\frac{\text{mole}}{\text{m}^2\ \text{sec atm}}\right]$
Ag-1	204	2.4×10^{-10}
Ag-2	204	5.0×10^{-9}
Ag-3	48	2.2×10^{-12}
Ag-4	77	1.1×10^{-10}
Au-1	270–290	3.2×10^{-5}
Au-2	280–305	1.8×10^{-7}
$(VO_2)_x$	177	1.0×10^{-10}

CONCLUSIONS

This work has demonstrated that by careful choice of the experimental conditions it is possible to follow quantitatively the rate of the exchange reaction (1) at the surface of supported metal and metal oxide catalysts, which possess drastically different selectivity in the oxidation of ET by O_2. The method employed has given an insight on the nature of ET adsorption and demonstrated its important role on the depth of oxidation of the olefin. A simple manner to distinguish among ET adsorptions is by the number of surface sites involved per ET molecule. This heuristic scheme gives a satisfying account of the contribution of ET adsorption to catalyst selectivity. The possibility of bringing into proper focus the role of ET adsorption on catalyst selectivity is the most interesting result of this work. In addition, this study has shown that, contrary to a prevalent view, ETO may be formed by reaction between ET and monoxygenated donor. Thus, molecular adsorbed oxygen is a sufficient but not a necessary requirement for the production of ETO from ET. Mechanistic reaction schemes, which require the presence of $O_2(s)$ may be valid in the presence of molecular O_2, but information on the adsorption process derived from them cannot be generalized without caution.

ACKNOWLEDGMENTS

One of us (G.M.) is grateful to the management of SNAM Progetti S.p.A. for financial support which made this work possible. Financial assistance from Grant GK-2013 of the National Science Foundation is gratefully acknowledged.

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