The Effect of Dichloroethane Moderation on the Adsorbed Species Present during the Oxidation of Ethylene over Silver

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Ethylene oxidation has been studied on a silver catalyst moderated by exposure to dichloroethane. Consistent with previous studies, it has been found that moderation causes a reduction in the oxidation rate and an increase in the selectivity towards ethylene oxide over that observed for an unmoderated catalyst. Infrared spectra have shown that moderation causes a reduction in the adsorption of ethylene and an enhancement in the adsorption of ethylene oxide and carbon dioxide. The effects of moderation have been interpreted in terms of a reaction mechanism proposed previously to explain ethylene oxidation over an unmoderated catalyst.

INTRODUCTION

It is well known that the selectivity of a silver catalyst used for the oxidation of ethylene to ethylene oxide is enhanced by the adsorption of chlorine on the catalyst surface (*1*). Such moderation is accomplished most frequently by the addition of small amounts of dichlorethane to the reactants. The dichloroethane adsorbs onto the silver and decomposes, thereby producing chloride ions (*2, 3*). Although the means by which an improvement in selectivity is brought about has not been established, it has been proposed (*2, 4, 5*) that the chloride ions strongly influence the form in which oxygen is adsorbed. Kilty *et al.* (*4*) have recently presented data which suggest that the dissociative adsorption of oxygen at 100°C can be completely suppressed by adsorption of a quarter of a monolayer of chloride ions. The adsorption of oxygen in a molecular form appears not to be affected by chloride coverages of

a quarter monolayer or less but does decline at higher coverages. On the basis of these results it is argued that even at reaction temperatures (200–300°C) chloride adsorption will influence the ratio of molecularly to dissociatively adsorbed oxygen. If it is further assumed that epoxidation occurs via the reaction of ethylene with molecularly adsorbed oxygen and combustion by reaction with atomically adsorbed oxygen, then the influence of adsorbed chloride ions on selectivity can easily be interpreted (*4–6*).

In a recent study by the present authors (*7*), it was shown that the evidence in support of the assumption that molecularly adsorbed oxygen is responsible for epoxidation is not sufficiently strong to exclude alternative assumptions. Working on the basis of surface structures deduced from infrared spectra taken under reaction conditions and rate data, it was concluded that plausible mechanisms for both epoxidation and combustion could be proposed involving only atomically adsorbed oxygen.

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The present study was undertaken to investigate the effects of dichloroethane moderation on the rates of epoxidation and combustion and the nature of the adsorbed species formed on the catalyst surface. Structures of the adsorbed species were established through an interpretation of their infrared spectra. A comparison of the reaction rates and surface structures associated with moderated and unmoderated catalyst was performed, and the results were reviewed in the light of the oxidation mechanism proposed in our previous paper (7).

EXPERIMENTAL METHODS

Since the catalyst and experimental apparatus used for this work have been described previously (7, 8), only brief mention of each will be given here. The catalyst consisted of a 6.6% loading of silver on Cab-O-Sil M-5. About 200 mg of this material was pressed into a disk $1\frac{1}{8}$ in. in diameter. To allow for a measurement of the disk temperature, a very small copper-constantan thermocouple was imbedded into the disk.

The principal component of the experimental apparatus was a heated infrared cell which was located in the sample compartment of a Perkin Elmer 457 spectrometer. The catalyst disk was supported within the cell so that it was aligned with the sample beam of the spectrometer. A second disk, consisting of pure Cab-O-Sil, was held in the reference beam. Using this technique it was possible to record the spectrum of only those species adsorbed on the catalyst and to subtract out the spectrum of the silica support and of reactants and products present in the gas phase.

The balance of the apparatus consisted of a gas recycle loop, of which the infrared cell is a part; a vacuum system to evacuate the cell; and a gas feed system to fill the recycle loop. The gas in the recycle loop was recirculated using a metal bellows

pump and its composition was measured by gas chromatography.

Two types of experiment were performed. The first, identified as adsorption runs, were carried out by flowing a mixture of ethylene and oxygen in helium into and out of the recycle loop while recirculating the gas in the loop. With this mode of operation the residence time of the reactants in the recycle loop was too short to allow for a measurable conversion of products. The spectra recorded during the adsorption runs were thus characteristic of the adsorption of reactants only. In the second set of experiments the reactants were recirculated without flow into and out of the loop. Under these circumstances the appearance of products could be observed and followed in time.

Prior to each run, a sequence of steps was used to prepare the catalyst. First, the catalyst was heated for 18 hr at 250°C in a vacuum of about 10^{-6} Torr. Next, the catalyst was reduced for 6 hr at 250°C in a recirculating stream containing 12% hydrogen in helium. At the end of this step, the hydrogen containing gas was removed and the catalyst was considered to be ready for use. For those runs in which a moderated catalyst was to be used, the catalyst was exposed to a recirculating mixture of 8.2% 1,2-dichloroethane in helium for a period of 1 hr at 220°C. During this step, the dichlroethane decomposed leaving behind chloride ions adsorbed on the surface of the catalyst. No measurement was made of the amount of chloride deposited onto the catalyst.

RESULTS AND DISCUSSION

Figures 1 and 2 illustrate a comparison of the spectra obtained for adsorption runs conducted at 170 and 220°C with and without catalyst moderation. For the unmoderated catalyst, four distinct bands are observed at 3130, 3090, 3020, and 2980 cm^{-1}. Moderation of the catalyst leads to a spectrum similar to that for the unmoderated

TABLE 1

Assignment of Infrared Bands to Surface Structures

$v(\text{cm}^{-1})$		Structure	
Unmoderated	Moderated		
3130	3130		
3090	3060		
3020	3020	$CH_2=CH_2$	
—	2995	$\vert$	(I)
2980	2960–2970	Ag^+	
—	2930–2950		
2270	2270	structure (II)	(II)
2350	2350	$O=C=O$ bonded to Ag	(III)
1365	1380		
1230	1215		
1035	1050	(IV) and	(V)
810	—		
605	615		
2970	2970		
2920	2920		
2890	2860	(VI) and	(VII)
2820	2830		
1080	—		
860	865		

catalyst but less intense. The second and fourth bands are shifted downscale to 3060 and 2965 cm^{-1}, respectively. In addition, two very weak bands appear at 2995 and 2940 cm^{-1}. Similar weak bands have been noted (7) at 3000 and 2950 cm^{-1} in some of the spectra taken with unmoderated catalyst samples. The resolution of the weak bands from the stronger ones appears to be enhanced upon moderation.

Based upon our previous studies (7, 8), the bands observed in Figs. 1 and 2 can be assigned to C–H stretching vibrations oc-curring in ethylene adsorbed onto partially ionized silver sites (see Table 1). Further-more, to account for a total of six bands it was proposed (7) that on an unmoderated catalyst sample two forms of adsorbed ethylene might be present, the first con-tributing bands at 3130, 3020, and 2980 cm^{-1}, and the second at 3090, 3000, and 2950 cm^{-1}. The ethylene adsorbed in the second form was postulated to be reactive based upon variations in the intensity of the band at 3060 cm^{-1} as reaction pro-ceeded. A similar interpretation can be

TABLE 2

Reaction Rates and Selectivity as a Function of Gas Composition and Temperature

Run no.	T (°C)	t (hr)	P_{O_2} (atm)	$P_{C_2H_4}$ (atm)	$P_{C_2H_4O}$ (atm)	P_{CO_2} (atm)	P_{H_2O} (atm)	$r_{C_2H_4O}$ (µmol/g Ag min)	r_{CO_2} (µmol/g Ag min)	$S_{C_2H_4O}$ (%)
R-9 (unmod.)	220	0	0.383	0.177	0.0	0.0	0.0	—	—	—
		1	0.376	0.171	0.004	0.010	0.010	155.6	332.3	48.4
		5	0.318	0.142	0.018	0.039	0.039	101.3	205.5	49.7
		9	0.278	0.115	0.028	0.059	0.059	63.1	108.5	53.8
		14	0.254	0.101	0.039	0.074	0.074	31.9	53.8	54.8
		18	0.247	0.097	0.041	0.078	0.078	16.6	23.6	58.4
R-14 (mod.)	220	0	0.383	0.177	0.0	0.0	0.0	—	—	—
		1	0.379	0.173	0.001_5	0.002_3	0.002_3	55.1	67.4	62.2
		5	0.361	0.161	0.002_1	0.005_1	0.005_1	36.4	46.6	61.0
		9	0.348	0.156	0.002_6	0.007_3	0.007_3	24.4	35.0	58.3
		14	0.326	0.148	0.003_1	0.010_2	0.010_2	15.2	24.8	55.1
R-10 (unmod.)	170	0	0.287	0.118	0.0	0.0	0.0	—	—	—
		2	0.275	0.112	0.003_2	0.006_9	0.006_9	49.0	106.8	47.8
		4	0.265	0.106	0.005_9	0.012_9	0.012_9	41.3	94.2	46.7
		6	0.253	0.099_8	0.008_0	0.017_2	0.017_2	31.2	57.7	52.0
		8	0.245	0.095_7	0.009_6	0.019_7	0.019_7	20.6	33.5	55.2
		11	0.237	0.091_6	0.010_7	0.021_6	0.021_6	8.4	14.2	54.2
R-15 (mod.)	170	0	0.287	0.118	0.0	0.0	0.0	—	—	—
		1	0.281	0.115	0.001_8	0.004_3	0.004_3	26.1	30.2	63.5
		3	0.274	0.109	0.002_3	0.006_2	0.006_2	15.2	20.2	60.2
		6	0.269	0.105	0.002_7	0.007_1	0.007_1	5.3	7.7	58.0

given for the spectra recorded with the moderated catalyst. In this instance, the less reactive form of adsorbed ethylene would be associated with the bands at 3130, 3020, and 2980, and the more reactive form would be associated with the bands at 3060, 2995, and 2940 cm^{-1}.

Reaction runs were performed at 170 and 220°C with both an unmoderated and a moderated catalyst. The product composition, reaction rates, and selectivity to ethylene oxide for these runs are given as a function of reaction time in Table 2. For the same initial gas composition, the rates of epoxidation and combustion are both significantly smaller over the moderated catalyst than over the unmoderated catalyst, but the selectivity associated with the moderated catalyst is higher. The variation of selectivity with extent of reaction also depends upon whether or not the catalyst is moderated. Runs R-9 and R-10 show an increase in selectivity during the run while runs R-14 and R-15 show a decline in
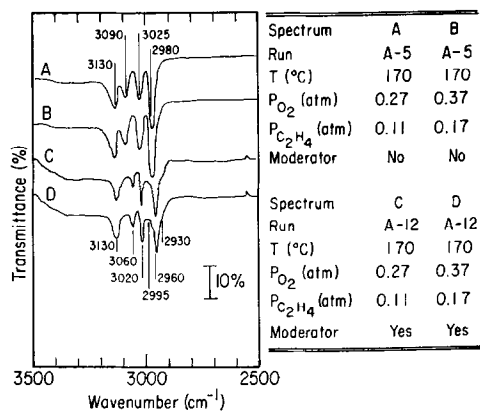

FIG. 1. Spectra of ethylene adsorbed in the presence of oxygen: $T = 170$°C.

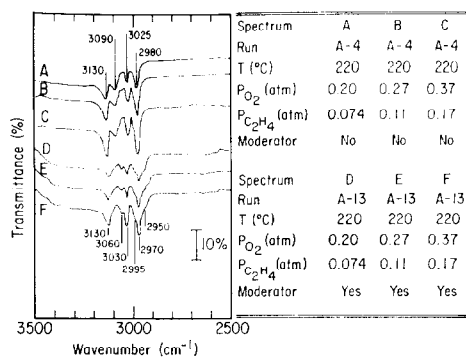| Spectrum	A	B	C
Run	A-4	A-4	A-4
T (°C)	220	220	220
P_{O_2} (atm)	0.20	0.27	0.37
$P_{C_2H_4}$ (atm)	0.074	0.11	0.17
Moderator	No	No	No
Spectrum	D	E	F
Run	A-13	A-13	A-13
T (°C)	220	220	220
P_{O_2} (atm)	0.20	0.27	0.37
$P_{C_2H_4}$ (atm)	0.074	0.11	0.17
Moderator	Yes	Yes	Yes

FIG. 2. Spectra of ethylene adsorbed in the presence of oxygen: $T = 220°C$.

selectivity. Furthermore, it is observed that the relative decline in reaction rates with reaction time is greater for the moderated catalyst than for the unmoderated catalyst. This last result is particularly surprising since the overall extent of reactant conversion is smaller for the runs performed with the moderated catalyst.

A comparison of the spectra, recorded during runs R-10 and R-15, is shown in Fig. 3. It is apparent that the spectra for the two runs are quite similar. Because of this similarity it is possible to assign the bands appearing in the spectra for run R-15 using the interpretations of the spectra for an unmoderated catalyst given previously (8). Table 1 illustrates the structures of the adsorbed species assigned to particular sets of bands. The only band appearing in the spectra but not shown in Table 1 is that

occurring at 1730 cm^{-1}. This band corresponds to the vibration of C=O groups in the partially oxidized intermediates which precede the formation of carbon dioxide and water.

Careful inspection of Fig. 3 reveals that the bands associated with the carbonate species (structures IV and V) and the alkoxide species (structures VI and VII) are more intense in spectra D through F than they are in spectra A through C. This observation is particularly surprising when it is further recognized that the gas phase partial pressure, of carbon dioxide and ethylene oxide, the two products which contribute to the formation of the carbonate and alkoxide structures respectively (8), are substantially lower for spectra D through F than for spectra A through C.

The evidence just presented suggests that moderation of the catalyst causes a stronger adsorption of reaction products than is observed on an unmoderated catalyst. This conclusion is consistent with the rapid decline in the rates of epoxidation and combustion associated with run R-15. In previous studies conducted with an unmoderated catalyst (7), it was noted that a rapid decline in the reaction rates was always brought about by exposure of the catalysts to high concentrations of either carbon dioxide or ethylene oxide. The latter product was found to be partic-
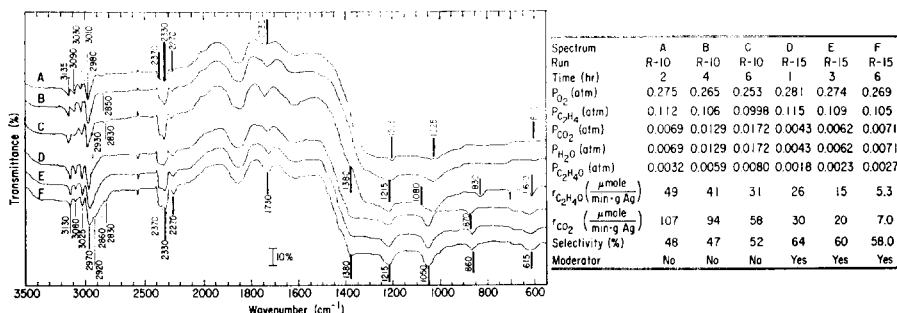

Spectrum	A	B	C	D	E	F
Run	R-10	R-10	R-10	R-15	R-15	R-15
Time (hr)	2	4	6	1	3	6
P_{O_2} (atm)	0.275	0.265	0.253	0.281	0.274	0.269
$P_{C_2H_4}$ (atm)	0.112	0.106	0.0998	0.115	0.109	0.105
P_{CO_2} (atm)	0.0069	0.0129	0.0172	0.0043	0.0062	0.0071
P_{H_2O} (atm)	0.0069	0.0129	0.0172	0.0043	0.0062	0.0071
$P_{C_2H_4O}$ (atm)	0.0032	0.0059	0.0080	0.0018	0.0023	0.0027
$r_{C_2H_4O} \left(\frac{\mu mole}{min \cdot g\ Ag} \right)$	49	41	31	26	15	5.3
$r_{CO_2} \left(\frac{\mu mole}{min \cdot g\ Ag} \right)$	107	94	58	30	20	7.0
Selectivity (%)	48	47	52	64	60	58.0
Moderator	No	No	No	Yes	Yes	Yes

FIG. 3. Comparison of spectra taken during reaction runs over unmoderated and moderated catalysts: $T = 170°C$.

ularly capable in causing a reduction of catalyst activity.

In order to discuss the effects of chloride moderation on enhancing the selectivity towards ethylene oxide, it is helpful to review first the oxidation mechanism which we have proposed (7) for an unmoderated catalyst.

1. $O_2 + 2Ag$ (or $Ag^{\delta+}$) $\rightleftarrows 2Ag^+O^-$

2. $O_2 + Ag$ (or $Ag^{\delta+}$) $\rightleftarrows Ag^+O_2^-$

3. $Ag^+O_2^- + Ag$ (or $Ag^{\delta+}$) $\rightleftarrows Ag^+O^-$

4. $Ag^+O^- + Ag$ (or $Ag^{\delta+}$) $\rightleftarrows Ag_2^+O^{2-}$

5. $C_2H_4 + Ag^{\delta+} \rightleftarrows Ag^{\delta+}C_2H_4$

6a. $C_2H_4 + Ag^+O^- \rightarrow Ag^+O^-CH_2CH_2\cdot$

6b. $C_2H_4 + Ag^+O^- \rightarrow Ag^+O^-\dot{C}HCH_3$

7a. $Ag^{\delta+}C_2H_4 + Ag^+O^- \rightarrow$
$$Ag^+O^-\dot{C}H_2CH_2 + Ag^{\delta+}$$

7b. $Ag^{\delta+}C_2H_4 + Ag^+O^- \rightarrow$
$$Ag^+O^-\dot{C}HCH_3 + Ag^{\delta+}$$

8. $Ag^+O^-CH_2CH_2\cdot \rightarrow Ag^+O^-\dot{C}HCH_3$

9. $Ag^+O^-\dot{C}HCH_3 + 5Ag^+O^- \rightarrow$
$$6Ag^+ + 2CO_2 + 2H_2O$$

10. $C_2H_4O + Ag$ (or $Ag^{\delta+}$) $\rightleftarrows$
$$Ag^+O^-CH_2CH_2\cdot$$

11. $CO_2 + Ag^{\delta+} \rightleftarrows Ag^{\delta+}CO_2$

12. $CO_2 + Ag^+O^- \rightleftarrows Ag^+CO_3^-$

13. $CO_2 + Ag^+O^- + Ag$ or $Ag^{\delta+}$) $\rightarrow$
$$Ag_2^+CO_2^{2-}$$

14. $H_2O + Ag^+O^- + Ag^{\delta+} \rightleftarrows 2Ag^+OH^-$.

Reactions 1 through 4 summarize the steps believed to occur when oxygen is adsorbed. Two types of adsorption sites are indicated. These are designated by Ag if the site is totally uncharged and by $Ag^{\delta+}(0 \leq \delta \leq 1)$ if the site carries a partial positive charge. The $Ag^{\delta+}$ sites are formed at silver positions adjacent to sites on which oxygen is adsorbed. Ethylene adsorption occurs exclusively on the $Ag^{\delta+}$ sites as

indicated by reaction 5. Two pathways are shown for the oxidation of ethylene, reactions 6 and 7. To explain the observed trends in selectivity with product and reactant concentrations, it was postulated that reaction 6a is favored over 6b and that reaction 7b is favored over 7a. The formation of ethylene oxide occurs by the reverse of reaction 10, and the formation of carbon dioxide and water by reaction 9. Once present in the gas phase, ethylene oxide can adsorb by reaction 10. The initial surface structure formed via reaction 10 can then isomerize via reaction 8, yielding a precursor to combustion. Finally, reactions 11 through 14 account for the adsorption of carbon dioxide and water.

In the proposed mechanism the selectivity towards ethylene oxide is dictated by the relative rates of reactions 6a and 7b. Since reaction 7b involves two surface species, the rate of reaction 7b will be more sensitive to surface coverage than the rate of reaction 6a which involves only a single surface species. As a result, the mechanism predicts that the selectivity towards ethylene oxide can be enhanced by reducing the surface concentrations of adsorbed ethylene and O^- ions.

The mechanism of moderation by dichloroethane can now be interpreted as follows. Contact of the catalyst with dichloroethane leads to a fractional coverage of the surface by chloride ions. When the reaction mixture is passed over the catalyst the surface concentrations of chemisorbed C_2H_4 and O^- will be less than for an unmoderated catalyst, due to the loss in sites. This results in a reduction of the rates for both epoxidation and combustion. However, since reaction 6a is first order in surface species while reaction 7b is second order, the extent to which the rate of epoxidation is reduced should be less than the extent to which the rate of combustion is reduced. The net result is an expected increase in the selectivity towards ethylene oxide over the moderated catalyst.

Experimental support for the proposed interpretation can be found in Fig. 1, where it is observed that the concentration of adsorbed ethylene is lower on a moderated than an unmoderated catalyst. While no measurements were made of the concentration of adsorbed oxygen, the work of Meisenheimer and Wilson (2) and Kilty *et al.* (4) clearly indicate that moderation by chloride ions causes a decrease in the amount of oxygen coverage.

In addition to altering the catalyst selectivity, moderation with dichloroethane causes an enhancement in the adsorption of reaction products. A possible explanation for this might be that the adsorbed chloride ions serve to increase the magnitude of δ associated with each $Ag^{\delta+}$ site above that which could be achieved by oxygen adsorption alone. If the $Ag^{\delta+}$ sites are preferred centers for product adsorption, this reasoning could explain the observed results.

As noted earlier, the strong adsorption of reaction products on the moderated catalyst appears to be the cause for the rapid decline in selectivity with increasing extent of reaction. An explanation for this observation can be provided in terms of the proposed mechanism. With an increase in the gas phase concentration of ethylene oxide, its adsorption via reaction 10 is enhanced and the concentration of adsorbed ethylene oxide is increased. Once present on the surface, the initial form of adsorbed ethylene oxide can isomerize via reaction 8 to form a precursor which enters into the combustion sequence. Therefore, the mechanism predicts that large concentrations of adsorbed ethylene oxide will contribute to a decline in the net rate of ethylene oxide formation and a concurrent increase in the rate of combustion. The overall effect is a decline in the selectivity.

CONCLUSIONS

The present work has shown that moderation of a silver catalyst by exposure to dichloroethane leads to a series of consequences: a reduction in the catalyst activity towards ethylene oxidation; an increase in the selectivity towards ethylene oxide; a decrease in the extent of adsorbed ethylene; and an increase in the adsorption of ethylene oxide and carbon dioxide. While the first two of these observations are consistent with prior investigations, the latter two observations are new. An interpretation for these results has been given in terms of a reaction mechanism proposed previously (7) to explain the oxidation of ethylene over an unmoderated catalyst. Central to the interpretation is the assumption that epoxidation occurs via reaction of gaseous ethylene and adsorbed oxygen (in the form of O^-) and that combustion occurs via reaction of adsorbed ethylene and oxygen. The effect of moderation is to adsorb chloride ions on the surface, thereby leading to a decrease in the surface concentrations of both adsorbed ethylene and oxygen. Since epoxidation is first order in surface species and combustion is second order, a decrease in the concentration of surface species leads to an increase in selectivity. In support of this interpretation is the reduction in ethylene adsorption with moderation noted in the present studies and the reduction in oxygen adsorption with moderation noted in the literature (2–4).

The postulated mechanism also permits one to explain the observed decline in selectivity of the moderated catalyst, as the concentration of reaction products in the gas phase increases. The enhancement in ethylene oxide adsorption caused by moderation drives the sequence of reactions which leads to a combustion of ethylene oxide. As as result, the formation of carbon dioxide and water occurs by both parallel and sequential pathways, leading to a decrease in selectivity.

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