

## Interaction of Dichloroethane and Oxygen with the Silver (110) Surface<sup>1</sup>

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In this work, the reaction of 1,2-dichloroethane on the Ag(110) surface was examined using a LEED-Augur system. The interaction of dichloroethane with an oxygen covered silver surface and the effect of chlorine adsorbed on silver on the oxygen chemisorption were investigated. An isolation valve permitted the exposure of the sample at pressures up to 1 Torr. Adsorbed oxygen is removed by dichloroethane, while different coverages of adsorbed chlorine are not affected when exposed to oxygen. Oxygen adsorption is completely inhibited when the chlorine coverage reaches  $4.2 \times 10^{14}$  atoms/cm<sup>2</sup>. The results show that chlorine and oxygen coexist on the surface mainly in separate domains, each with its own structure. The presence of chlorine, however, seems to affect appreciably the silver-oxygen bond.

### INTRODUCTION

The mechanism of oxygen adsorption and desorption on the silver surface has been the object of many studies, because it is of fundamental importance for understanding the unique catalytic action of silver for oxidizing ethylene to ethylene oxide. It is well known that the selectivity of the silver catalyst for this reaction, with respect to the complete oxidation to carbon dioxide and water, is improved by the addition of small amounts of halogenated compounds in the gaseous phase. In most cases, dichloroethane has been employed for this purpose.

The interaction of dichloroethane with the silver surface and the effect of the adsorbed chlorine on the adsorption of oxygen on silver has been studied by Meisenheimer and Wilson (1). These authors found that, at sufficiently high temperatures, dichloroethane decomposes on silver,

yielding gaseous ethylene and adsorbed halogen on the surface. The effect of preadsorbed chlorine on the oxygen adsorption was a strong decrease of the adsorption rate.

Kilty *et al.* (2) found that preadsorption of chlorine reduces the amount of oxygen subsequently adsorbed on polycrystalline silver. In particular, chlorine, up to a coverage of about  $3 \times 10^{14}$  atoms/cm<sup>2</sup>, inhibits the dissociative adsorption of oxygen, thus permitting only the adsorption of undissociated molecules, which are considered to be responsible for the oxidation of ethylene to ethylene oxide. They also found that a coverage of about  $5.5 \times 10^{14}$  atoms/cm<sup>2</sup> of chlorine completely inhibits any oxygen adsorption on silver.

In previous studies (3-5), conducted in our laboratory, the structure and stability range of the adsorption layers formed by oxygen and chlorine on the low-index faces of silver single crystals were studied with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), thermal

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desorption, and work-function measurements.

The study of adsorption-desorption processes on single crystal faces, that is, on systems with a well-defined geometry, by means of experimental techniques that give specific information on an atomic scale may be an essential step in acquiring a better and more detailed knowledge of the basic mechanisms of simple catalytic processes.

The goal of the present work was to obtain more information, on an atomic scale, about the interaction of dichloroethane and oxygen on a (110) silver surface, to study the effect of adsorbed chlorine on oxygen chemisorption, and to compare the results with those obtained by other authors for polycrystalline materials.

The (110) face was selected for this study because both chlorine and oxygen form more than one ordered phase at different coverages. The different phases of the same atomic species are characterized by different thermal stabilities. Although the structures proposed for these two-dimensional phases (4, 5) must still be considered as tentative models, they nevertheless indicate that different adsorption states exist, depending on the coverage, on the same surface geometry.

In this paper, the results of our study on the interaction of 1,2-dichloroethane with the silver surface will be presented first, and the results of previous work concerning oxygen chemisorption will be briefly reviewed. Then the interaction of dichloroethane with preadsorbed oxygen and vice versa will be examined.

#### EXPERIMENTAL

The experimental apparatus and procedures used have been described previously (3, 4).

Briefly, the apparatus consists of a standard three-grid LEED-Auger system in which the atmosphere could be varied, in a well-controlled way, from  $5 \times 10^{-10}$

Torr to about 1 Torr of a given gas, using a sample isolation valve for pressures higher than  $10^{-3}$  Torr. The sample temperature was varied by indirect heating and measured with a Pt-Pt/Rh thermocouple. The gas composition was monitored with a quadrupole mass spectrometer. The silver single crystal (6 N purity) was cut parallel to the (110) plane to within  $1^\circ$ .

#### RESULTS AND DISCUSSION

*Adsorption of dichloroethane.* After a few minutes' exposure of the sample to dichloroethane vapors at pressures of the order of  $10^{-2}$  Torr and at temperatures from 100 to  $250^\circ\text{C}$  an ordered  $\text{C}(4 \times 2)\text{-Cl}$  superstructure [see ref. (6) for nomenclature] was formed. The Auger spectrum indicated that only chlorine was present on the silver surface, so carbon does not assist in forming this surface phase. This ordered layer corresponds to the maximum chlorine coverage observed in our conditions on the silver (110) surface. It has been considered (4) as a "corrosion" layer and its structure has been tentatively interpreted as a distorted hexagonal packing of both chlorine and silver atoms, forming a two-dimensional chloride, with a structure similar to that of the (111) planes of bulk silver chloride. If this model is correct this surface phase corresponds to a coverage of  $6.4 \times 10^{14}$  chlorine atoms/cm<sup>2</sup>, which is almost the same maximum coverage found also on the (100) and (111) silver faces (4).

At lower exposures to dichloroethane, or by removing, in part, the chlorine from the  $\text{C}(4 \times 2)$  superstructure, a  $(2 \times 1)$  superstructure was observed. The latter is probably a reconstructed layer with one chlorine atom for every two silver atoms, thus corresponding to a coverage of  $4.2 \times 10^{14}$  chlorine atoms/cm<sup>2</sup>. No other ordered structure, due to chlorine chemisorption, was observed on the silver (110) surface. Both of the observed structures seem to be stable at the temperatures of catalytic interest. The  $\text{C}(4 \times 2)$  phase is

stable in the ultrahigh vacuum up to at least 250°C, while the  $(2 \times 1)$  phase is stable up to much higher temperatures (4).

After exposure of the sample to dichloroethane at room temperature, AES indicates the presence of both chlorine and carbon on the surface. In Fig. 1, the Auger spectra of the clean surface and of the surface after exposure to dichloroethane are shown. The peak at about 180 eV is due to chlorine. The carbon Auger KLL peak is expected at about 270 eV, but it cannot be resolved from the  $M_{4,5}N_1N_{4,5}$  peak of silver at 264 eV because the two peaks are very broad. Therefore, the presence of small amounts of carbon can only be inferred from variation in the line shape of the silver peak. The peak height ratio between the 264 and the 300 eV silver peaks (using a 5 V rms modulation at the second grid) is 0.48 for the clean surface and 0.55 for the sample after adsorption. About one-third of a monolayer of carbon, corresponding to the latter ratio, is indicated by an

approximate analysis. The chlorine coverage, according to the evaluation made in the previous work (4), corresponds to a half-monolayer, that is, to  $4 \times 10^{14}$  atoms/cm<sup>2</sup>. At this surface composition, a  $(2 \times 1)$  superstructure was formed, which is also observed when only chlorine is present on the surface.

The results, obtained for the interaction of dichloroethane with the silver (110) surface, are in general agreement with those of Meisenheimer and Wilson (1). That is, at temperatures above 100°C, the dichloroethane rapidly decomposes on the silver surface leaving only chlorine adsorbed. We were not able, however, to confirm whether the organic part of the molecule desorbs as ethylene. Meisenheimer and Wilson stated also that dichloroethane is completely adsorbed at room temperature. Our results, however, seem to indicate that the dichloroethane is dissociated, at least in part, into chlorine atoms, giving a surface two-dimensional

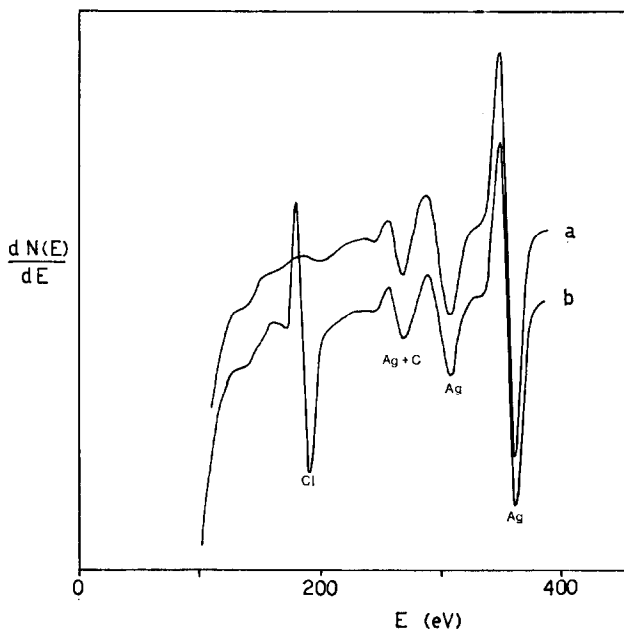


FIG. 1. Auger spectra of a (110) silver surface (a) before and (b) after exposure to  $10^{-2}$  Torr dichloroethane at room temperature for 5 min. The primary beam energy was 2.5 KeV with a current of  $1 \mu\text{A}$ , at glancing incidence. Modulation, 5 V rms.

phase characteristic of chlorine atoms alone, and a residual organic group, which remains adsorbed. It is possible that the decomposition may be caused by the electron beam used for LEED or AES. Some trials made with AES, however, indicated that no variation of the surface composition or of the LEED diagram occurs whenever primary currents of the order of  $1 \mu\text{A}$  are employed.

*Adsorption of oxygen.* The surface phases formed from oxygen chemisorption on the (110) silver surface, their structure and stability, have been reported (5). The mechanism of the oxygen desorption from the (110) surface will be discussed elsewhere (7). In this section, the results obtained are briefly reviewed.

The surface phase corresponding to a maximum coverage of oxygen on the (110) silver surface was obtained by exposing the sample for a few minutes to  $10^{-2}$ – $10^{-1}$  Torr of oxygen, from room temperature up to  $250^\circ\text{C}$ . A well-ordered  $(2 \times 1)$  superstructure was formed, which is interpreted as a corrosion layer where both silver and oxygen atoms are disposed in a distorted hexagonal array. If this model is correct, the surface coverage is such that one oxygen atom is found for each silver atom of the clean surface. This two-dimensional oxide is stable up to the temperature where rapid desorption of oxygen is observed. Thermal desorption spectra of oxygen have a maximum at about  $280^\circ\text{C}$ .

A study of the kinetics of the desorption, made by using the variation of the LEED intensities and the desorption spectra (7), showed that oxygen desorbs directly from the immobile adsorption layer. The desorption kinetics can be approximately described as a second-order process. An activation energy of about 40 Kcal/mole was derived. Both the order of the process and the activation energy are in agreement with the results of Kollen and Czanderna (8).

At lower coverages, obtained by partially

desorbing the oxygen from the  $(2 \times 1)$ -O superstructure and allowing the surface layer to rearrange itself by annealing at temperatures just below the beginning of appreciable desorption (typically  $150^\circ\text{C}$ ), other ordered structures are observed of the type  $(n \times 1)$  with  $n > 2$ , corresponding to a decreasing coverage with increasing  $n$ . When the surface is covered only in part by the  $(2 \times 1)$ -O phase, the  $(3 \times 1)$ -O phase is found to coexist with it.

The  $(n \times 1)$ -O structures correspond to a much lower oxygen content and have completely different characteristics from the  $(2 \times 1)$ -O. They apparently result from adsorption of oxygen atoms in the troughs of the (110) surface with one oxygen for every  $n$  atoms of silver. At  $150^\circ\text{C}$ , oxygen is completely mobile and probably moves along the troughs. This mobile oxygen desorbs rapidly at slightly lower temperatures than those for oxygen desorption from the  $(2 \times 1)$ -O superstructure.

After exposure at temperatures above  $300^\circ\text{C}$ , no oxygen-ordered phase is observed, but there is experimental evidence that oxygen penetrates below the silver surface. This oxygen is observed to desorb at temperatures higher than  $450^\circ\text{C}$ . The diffusion into the near-surface regions was also reported by Czanderna *et al.* (9).

Other authors [see, for instance, Refs. (2, 8, 10)] reported two kinds of adsorbed oxygen: dissociated and undissociated. On the basis of the studies of Czanderna and co-workers (8, 10), we concluded that the oxygen studied in our conditions was atomic. The undissociated oxygen should, in fact, desorb from the silver surface below  $100^\circ\text{C}$  (10). In our study we did observe a weak desorption at low temperatures on some samples. We were not able to demonstrate that this was due to the silver sample and not to the support. In any case, the amount desorbed was about one order of magnitude lower than the amount of oxygen that desorbs in the  $280^\circ\text{C}$  peak.

This is not in agreement with the above-cited authors, who found comparable amounts of molecular and atomic adsorbed oxygen after adsorption at 10 Torr on silver powder. The difference may result from the oxygen pressure or the sample employed.

*Interaction of dichloroethane with pre-adsorbed oxygen.* When the sample was exposed to oxygen, in order to form the  $(2 \times 1)\text{-O}$  structure, and then to dichloroethane vapors, the same ultimate conditions of the surface were obtained as for the direct exposure of the clean surface to dichloroethane. That is, AES indicates that only chlorine is present on the surface (at least when exposures to dichloroethane were made at temperatures of  $100^\circ\text{C}$  or higher), and the LEED diagram indicates that the  $\text{C}(4 \times 2)\text{-Cl}$  structure is formed. After such exposure to dichloroethane, no desorption of oxygen can be observed from the sample.

If the exposure to oxygen is made at temperatures over  $300^\circ\text{C}$ , the oxygen in or on the silver is not removed by dichloroethane, but the chlorine overlayer is always formed. AES indicates a weaker oxygen peak and desorption of oxygen at temperatures over  $450^\circ\text{C}$  can be observed.

The results show that oxygen adsorbed on the silver (110) surface is completely removed by interaction with dichloroethane. It is not possible, however, to state whether the adsorbed oxygen is displaced by the chlorine or is removed by reaction with the organic part of the molecule. The oxygen that remains on silver after reaction at high temperatures is not removed by interaction with dichloroethane. This agrees with the hypothesis that this oxygen is present below the silver surface, so that it does not interfere with the adsorption of chlorine on the surface.

*Adsorption of oxygen on the surface partially covered by chlorine.* Partial coverages of chlorine atoms were obtained by controlled exposure of a clean surface to

dichloroethane at  $150^\circ\text{C}$ , thus avoiding any carbon adsorption. The chlorine coverage was estimated by measuring the ratio between its Auger peak and the main silver peak ( $\text{M}_{4,5}\text{N}_{4,5}\text{N}_{4,5}$  transition) and taking  $6.4 \times 10^{14}$  chlorine atoms/cm<sup>2</sup> as the maximum coverage. The primary energy, modulation amplitude, and glancing incidence angle were kept the same for these measurements.

The sample, with partial coverages of chlorine, was then exposed to  $10^{-1}$  Torr of oxygen at  $150^\circ\text{C}$  for 5 min. At this exposure, full oxygen coverage is obtained on the clean surface. In Fig. 2, a series of oxygen desorption spectra from surfaces with different amounts of chlorine is shown. With increasing chlorine coverage, the amount of desorbed oxygen decreases. With a chlorine coverage of  $4.2 \times 10^{14}$  atoms/cm<sup>2</sup>, or higher, oxygen desorption can no longer be observed. This is shown better in Fig. 3, in which the amount of oxygen desorbed (measured as the area under the desorption peak) is plotted as a function of the chlorine coverage. The Auger spectra are in agreement with these results. However, there was a large uncertainty in the determination of the oxygen peak heights because very low primary

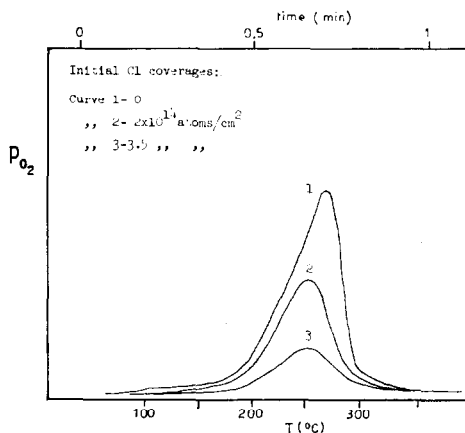


Fig. 2. Desorption spectra of oxygen adsorbed on a (110) silver surface with different coverages of chlorine.

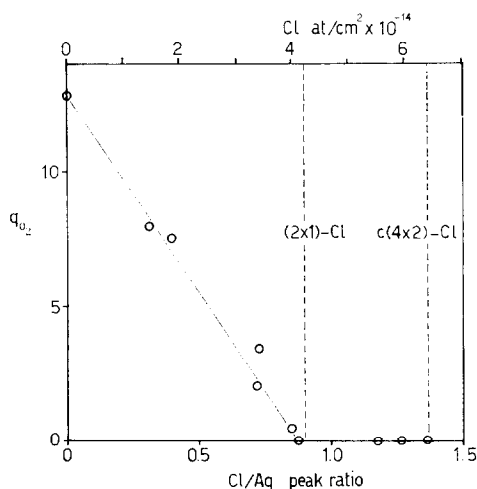


FIG. 3. Amount of oxygen ( $q_{O_2}$ , arb. un.) desorbed from the sample as a function of the coverage of preadsorbed chlorine (upper scale) or of the chlorine-to-silver Auger peak ratio (lower scale).

currents had to be employed in recording the Auger spectra to limit the electron beam effect on the surface composition.

If a surface completely covered by the  $(2 \times 1)$ -Cl superstructure is exposed to  $10^{-1}$  Torr of oxygen at temperatures above  $300^\circ\text{C}$ , a considerable amount of oxygen is indicated by AES, and desorption of oxygen over  $450^\circ\text{C}$  is observed. Thus

absorption of oxygen into the silver through the  $(2 \times 1)$ -Cl overlayer is still possible in these conditions.

The surface phases found by LEED at various Cl/Ag peak ratios are listed in Table 1. The  $(2 \times 1)$ -O structure, when present with the  $(2 \times 1)$ -Cl structure, is indicated by sharper  $(h \pm \frac{1}{2}, k)$  spots, which are usually diffuse for the  $(2 \times 1)$ -Cl structure. Moreover, intensity maxima of the two  $(2 \times 1)$  structures are observed at different energies. The latter consideration also permits the  $(2 \times 1)$ -O to be recognized when it and the  $(4 \times 1)$ -O are both present.

The results reported in Table 1 are in agreement with those found by thermal desorption and AES; that is, no oxygen remains chemisorbed in our experimental conditions when the surface is completely covered by the  $(2 \times 1)$ -Cl or the  $C(4 \times 2)$ -Cl structures (i.e., at a coverage of  $4.2 \times 10^{14}$  chlorine atoms/cm<sup>2</sup> or higher). At lower coverages, the LEED results indicate that oxygen chemisorbs in domains with long-range order. These domains have the same structures as those found with only oxygen on the surface. The chlorine atoms are also adsorbed in domains, but of

TABLE 1  
SURFACE STRUCTURES AFTER ADSORPTION OF OXYGEN ON THE (110) SILVER  
SURFACE WITH DIFFERENT COVERAGES OF CHLORINE

Cl/Ag peak ratio	Cl atoms/cm <sup>2</sup> $\times 10^{-14}$	Structures observed with LEED		
		Chlorine phases		Oxygen phases
		Before oxygen exposure	After oxygen exposure	
1.37	6.4	$C(4 \times 2)$ -Cl	$C(4 \times 2)$ -Cl	—
0.87	4.2	$(2 \times 1)$ -Cl	$(2 \times 1)$ -Cl	—
0.72	3.4	$(2 \times 1)$ -Cl	$(2 \times 1)$ -Cl	$(2 \times 1)$ -O weak + $(4 \times 1)$ -O strong
0.40	1.8	—	—	$(2 \times 1)$ -O strong + $(5 \times 1)$ -O weak
0.30	1.4	—	—	$(2 \times 1)$ -O

smaller dimensions or with shorter range order, which are not affected by the oxygen adsorption.

The  $(2 \times 1)$ -O structure is almost always observed and is stable up to the temperature of oxygen desorption. The  $(3 \times 1)$ -O structure has not been observed in the presence of chlorine, and only  $(n \times 1)$  structures with  $n > 3$  have been found to coexist with the  $(2 \times 1)$  structure. These  $(n \times 1)$ -O superstructures, in the presence of chlorine, are observed to disappear on heating at temperatures of 110–120°C and reappear on cooling. As reported before, this phenomenon was also observed for oxygen alone, but at higher temperatures, that is, at about 150°C, and was attributed to a complete disordering of the structure, corresponding to a high mobility of oxygen atoms on the silver surface.

Our observations strongly indicate that, below the coverage corresponding to the  $(2 \times 1)$ -Cl structure, chlorine and oxygen are present on the surface mainly in separate domains, each with its own structure. This may be attributed to a sufficient mobility of the surface atoms at the temperatures considered, so that separate domains are likely to exist even at the temperatures of catalytic interest. The presence of chlorine, however, affects significantly the oxygen-silver interaction, since the  $(n \times 1)$  structures with  $n > 2$  disappear reversibly at temperatures lower than those observed for oxygen alone. Thus, a partial coverage of chlorine seems to lower significantly the temperature at which oxygen adsorbed in the  $(n \times 1)$  structures (with  $n > 2$ ) becomes mobile. This may be correlated with the observed decrease in the temperature of desorption. Figure 2 indicates that the oxygen desorption temperature is slightly decreased with increasing chlorine coverage. This decrease is, however, difficult to ascribe only to the presence of chlorine, since a similar decrease has been observed even without chlorine at low oxygen coverages and has been

ascribed to different adsorbed states of oxygen at different coverages, corresponding to the structures observed with LEED (?). In the presence of chlorine, however, the desorption occurs about 5–10°C lower than with oxygen alone. Therefore, an indirect effect of chlorine on the silver-oxygen bond must be considered, although the two atomic species appear to be adsorbed in separate domains. This may also account for the fact that, in the domains free of chlorine, the formation of the  $(n \times 1)$ -O structures with  $n > 3$  is favored with respect to the  $(2 \times 1)$ -O and the  $(3 \times 1)$ -O as the chlorine coverage increases.

Although no chemisorbed oxygen could be detected on the surface covered by the  $(2 \times 1)$ -Cl structure, oxygen atoms may penetrate below the silver surface, as observed after exposure at high temperatures. This indicates that oxygen can still interact with the chlorine covered surface for a sufficient amount of time to dissociate and diffuse into the near surface bulk regions.

It is doubtful whether the general mechanism proposed by Kilty *et al.* (2), that dissociative chemisorption of oxygen on silver requires four adjacent silver atoms so that one-fourth of a chlorine monolayer is sufficient to prevent dissociative adsorption, can be applied to interpreting our results on the (110) face. At complete coverage of the (110) surface with oxygen, only one surface phase is observed. Formation of this phase appears to be inhibited by chlorine adsorption, but it is still detectable up to a chlorine coverage of a half-monolayer. Other  $(n \times 1)$ -O structures are found to be favored when coverage of the surface by the chlorine domains increases, but formation of these structures is also completely inhibited at half-coverage of chlorine.

If the difference in our results and those of Kilty *et al.* (2) is not due to an effect of impurities, it should indicate a significant difference in the adsorption properties, and

probably the catalytic properties, of different crystal faces. Thus, it may be important to work on the single crystal surface, in order to acquire more specific information on particular catalytic mechanisms, as recently emphasized by Kahn, Petersen, and Somorjai (11).

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