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The Role of Chlorine in Oxygen Adsorption on Ag(111)

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The effect of chlorine adsorption on oxygen adsorption on Ag(111) was studied with HREELS and TPD. Oxygen adsorption on Ag(111) and Ag(111) exposed to a low chlorine dose produces mainly atomic oxygen species at 170 K and room temperature. On Ag(111) exposed to a high chlorine dose and a surface with the same chlorine adsorption conditions, but followed by removal of chlorine, a molecular oxygen species was the only product of oxygen adsorption at 170 K or room temperature. The altered behavior of oxygen adsorption is due to surface defects created via chlorine adsorption. It was also found that these surface defects increase the adsorption rate of oxygen and promote the diffusion of oxygen into the subsurface.

INTRODUCTION

Ag is a catalyst for two industrial processes: the epoxidation of ethylene to ethylene oxide and the selective oxidation of methanol to formaldehyde (*1*, *2*). In the epoxidation process, Cl is used as a promoter (*2–6*). Many aspects of the epoxidation process and Cl promotion are still unresolved (*2*). In the methanol dehydrogenation process, Cl is not usually acknowledged as a promoter. In methanol dehydrogenation, a form of Ag catalysts that is particularly selective is electrolytic Ag (*7*). If it is now supposed that it is the electrolysis that makes this form of catalyst especially desirable, and one form of electrolysis would be through the adsorption of Cl, then knowledge of how Cl adsorption affects Ag and its adsorption properties is important.

In a previous report (*8*), we presented a model of Cl adsorption on Ag(111) and the changes effected on the Ag surface. Here, we shall briefly describe these changes and further report on how Cl adsorption affects oxygen adsorption on the Ag surface. We also propose a mechanism by which Cl action occurs. A knowledge of how Cl adsorption affects oxygen adsorption is prerequisite to ideas on how Cl adsorption affects ethylene epoxidation and the selective oxidation of methanol. In later reports, we shall extend our work to the effect of Cl adsorption on these two reactions.

Unresolved issues in the epoxidation reaction include the identity of the useful surface oxygen species, whether it is atomic oxygen or molecular oxygen, and the role played by subsurface oxygen (*2*). In earlier work, roughly until the 1980s, most workers favored the suggestion by Worbs (*9*) that the active oxygen species in ethylene epoxidation is molecular oxygen. This suggestion received considerable supporting evidence from Kilty *et al.* (*10*), who detected molecular oxygen and its participation in a reaction at the double bond of ethylene by infrared spectroscopy under simulated reaction conditions. Other investigators (*4*, *5*, *11–13*) have argued for the molecular oxygen hypothesis by the deduction that it predicts a maximum selectivity of 6/7 to ethylene oxide and this selectivity was not exceeded. However, the 1980s saw a shift toward the view that it is atomic oxygen that is the reaction intermediate. Sev-

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eral authors (*14–16*) reported in 1983 and 1984 a selectivity toward ethylene epoxide that was higher than 85%, which directly disproves the prediction of the molecular oxygen hypothesis. In one case, this very high selectivity was later shown to be a non-steady-state selectivity (*2*), but it gave much impetus to the atomic oxygen viewpoint. Now, most of the evidence for the atomic oxygen hypothesis derives from surface science studies on model systems (*1*, *2*). We argue here that the conclusions drawn from these works are not necessarily directly transferable to industrial promoted catalysts. We show that a result of Cl adsorption is the creation of defect sites, and oxygen adsorption on these sites is different from oxygen adsorption on "smooth faces." If it is the case that these (defect) sites are important for reactions on Ag, then surface science works with "defect-free surfaces" would not be directly relevant.

Previous works on Cl adsorption have shown that Cl adsorption promotes room temperature adsorption of oxygen to adsorb in a molecular state. The standard reference work is possibly that of Kilty *et al.* (*10*), which gave direct spectroscopic evidence. Kilty *et al.* (*10*) gave the explanation that chlorine inhibits dissociative adsorption of oxygen by poisoning dissociative sites of ensembles of more than one Ag atom. Kamath *et al.* (*17*) also observed that oxygen is adsorbed molecularly in the singlet state on Ag foil containing preadsorbed chlorine. We report on a similar observation of Cl promotion of molecular oxygen adsorption. We add the observation that *Cl promotion does not require the continuing presence of Cl.*

Tan *et al.* (*18*) showed that coadsorbed chlorine enhances the surface to subsurface transport of chemisorbed oxygen on Ag(*111*). Our work here reports on a similar observation of Cl promotion of oxygen dissolution and adds a reason compatible with the enhancement of molecular oxygen adsorption.

EXPERIMENTAL

The apparatus and techniques are the same as had been described previously (*8*). In brief, it consists of an ultrahigh vacuum system with a base pressure of less than 3×10^{-10} mbar from Leybold. This has facilities for AES, LEED, HREELS, ISS, UPS, and quadrupole mass spectroscopy (QMS) for verification of the purity of inlet gases and TPD experiments. All the HREEL spectra involved in this study were tuned for a resolution of 80–120 cm^{-1} and were taken with a primary electron energy of 2.3 eV.

The Ag(111) sample was prepared by conventional mechanical polishing techniques and etched in a dilute $NH_3 : H_2O$ solution. This was mounted by 0.3-mm Ta wires through cuts on opposite sides of the sample onto Cu rods. The sample was cleaned by several cycles of 1500-eV Ar ion bombardment, oxidation in oxygen ($1-5 \times 10^{-7}$ mbar), reduction in hydrogen ($1-5 \times 10^{-7}$ mbar), and annealing to 823 K. Surface cleanness and structure were verified by AES, LEED, and HREELS. Sample temperatures were measured with a Pt–Pt/Rh thermocouple tied to the back of the sample.

A comment about the "goodness" of the Ag(111) surface should be clarified. Our surface is only nominally a (111) face. It does show a "good" (111) LEED pattern, but we have evidence (see below on its HREELS characterization and oxygen adsorption behavior) that it contains a fair amount of defect sites. We have shown that Cl adsorption results in the creation of defect sites (*8*), and after several rounds of high exposures of Cl adsorption these cannot be completely removed by annealing. We have chosen to work with this nominal (111) surface because our main interest is in Cl adsorption and oxygen adsorption on defect-free (111) faces is well documented (*1*, *2*). The alternative is to mechanically repolish the Ag crystal after every Cl adsorption experiment, which is unbearably inconvenient.

In this work, we used surfaces where we estimate the portion of the surfaces that is defects at 10–20%. This estimate is based on the assumption, made from our results, that the adsorption site for a stable form of molecular oxygen, which we term "O_2(stable)," is a defect site. We used the proportion of desorbed oxygen that is O_2(stable) as the estimate of the proportion of the surface that are defects. The role of these defects, in this context, is to serve as nucleation sites for the formation of AgCl crystallites. This prevents the formation of an epitaxial layer of AgCl that would have taken place on a defect-free surface. We have shown (*8*) that Cl adsorption on Ag(111) proceeds via three regimes (see Results section, paragraph 6). In the presence of defects, regime (b), which is an epitaxial layer of AgCl on Ag(111), does not form. Thus, by using a defective surface in this work we lose a look at the effect of Cl adsorption to regime (b) on oxygen adsorption. We have shown (*8*) that defects produced by Ar ion bombardment are also nucleation sites for the formation of AgCl. To reference this work to other works that could use defect-free surfaces, we believe the equivalent to our surface, for the type of results reported here, is a defect-free surface that is roughened by Ar ion bombardment to 10–20% roughness.

High purity oxygen used for adsorption was introduced through an effusive tube (3 mm o.d. × 1 mm i.d.) doser placed about 10 mm from the surface of the sample. Chlorine vapor was produced by the solid state electrolysis of an AgCl pellet in an electrochemical cell. The adsorption conditions for Cl to give different stages of chlorine adsorption are the same as previously described (*8*). All the preadsorptions of chlorine were carried out at room temperature. The exposures of oxygen were calculated from the uncorrected readings of an ion gauge and the adsorption time and corrected for dosing from a directed effusive source. We estimate that the effusive tube doser gives an exposure enhancement of about a factor of 7.

RESULTS

We studied oxygen adsorption by high resolution electron energy loss spectroscopy (HREELS) and temperature-programmed desorption (TPD). We first present results on oxygen adsorption on clean Ag(111). We then show the changes brought about by Cl preadsorption. We finally show oxygen adsorption on a Cl-modified Ag surface where the Cl was removed before oxygen adsorption. This Cl-modified surface was verified to be Cl-free by AES. We estimate our AES sensitivity to be better than 1%, that is, we estimate that Cl left on this surface amounted to less than 1%.

Figure 1 shows HREEL spectra for oxygen adsorption at ≈170 K on Ag(111) and with heating of the sample to room temperature. Figure 1a is the background spectrum from clean Ag(111). A plateau peak with a frequency of 700–800 cm^{-1} is evident. This is assigned to surface defects as was done previously (*8*, *19*). Briefly, the arguments for this assignment are by compar-

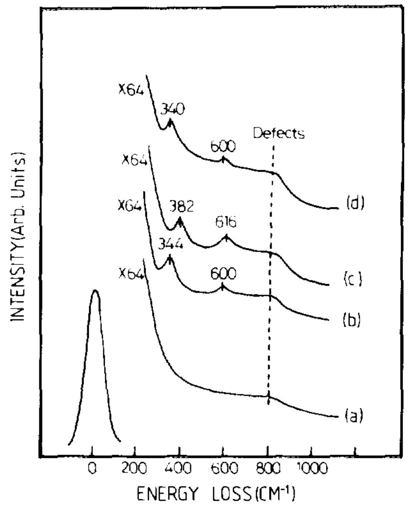

FIG. 1. HREEL spectra for (a) clean Ag(111), (b) after an oxygen exposure of 240 L at 170 K, (c) 480 L at 170 K, and (d) warming to room temperature.

ison with HREEL spectra from purposely-made-defective surfaces and LEED data. This assignment is consistent with the oxygen adsorption behavior described below as compared with published works on defect-free Ag(111) surface. Granted this assignment, this shows that a fair amount of defects are residual on our clean Ag(111) surface (see Experimental section).

The spectrum from oxygen adsorbed on Ag(111) at ≈170 K from an exposure of 240 L shows two vibrational peaks (Fig. 1b). Based on assignments in the literature (*19–21*) by Backx *et al.*, Sexton and Madix, and our previous works, the peak at 312–405 cm^{-1} is due to atomic oxygen (Ag–O stretch) and the peak at 600–640 cm^{-1} is due to molecular oxygen (O–O stretch of an oxygen molecule parallel to the surface). The molecular oxygen frequency is also in fair agreement with that reported by Kilty *et al.* (*10*). Thus, Fig. 1b shows that both atomic oxygen and molecularly oxygen exist on the surface. With the increase of oxygen exposure, the intensities of both peaks increase but especially that from the molecular oxygen species (Fig. 1c). When the sample was heated to 300 K, the height of the molecular oxygen peak was lowered (Fig. 1d), but the peak did not disappear completely. As compared with works on defect-free Ag(111) faces, and unpublished data from this Ag(111) sample as it was first put into the UHV system and after it was repolished and annealed, which show that molecular oxygen does not exist on Ag(111) above 200 K and that the sticking probability for oxygen is extremely low (ca. 10^{-5} to 10^{-6}), our surface showed two points of discrepancy: there is a small amount of molecular oxygen that is stable to 400 K and the sticking probability of oxygen is much higher. Both of these are due to the presence of surface defects (see Discussion section) and this is self-consistent with the assignment of surface defects in the previous paragraph.

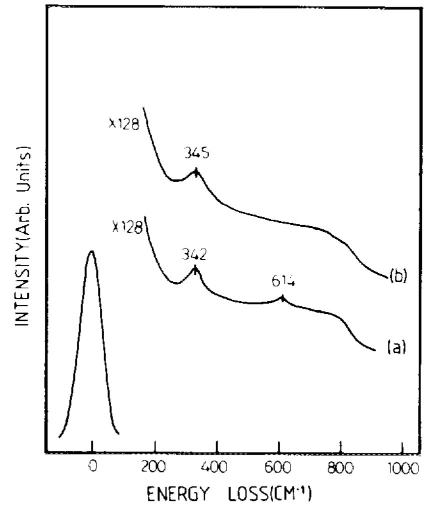

FIG. 2. HREEL spectra for oxygen adsorbed on Ag(111): (a) 6400 L at room temperature and (b) heating to 400 K.

Figure 2 shows the HREEL spectra of Ag(111)/O after an exposure of 6400 L oxygen at room temperature. It is shown that both atomic (342 cm^{-1}) and molecular oxygen (614 cm^{-1}) are present on the surface at room temperature (Fig. 2a). However, only atomic oxygen is seen on the surface after heating to 400 K, that is, this species of molecular oxygen desorbs by 400 K. The thermal desorption spectrum from a 6400 L oxygen adsorption on Ag(111) at room temperature is shown in Fig. 3. Two peaks at 380 and 520 K represent the desorptions of molecular oxygen and atomic oxygen, respectively, where these assignments are made following earlier workers (*22–27*).

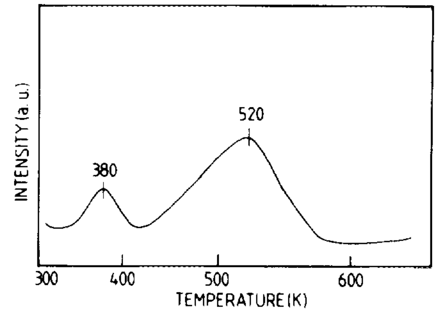

FIG. 3. TD spectrum from oxygen on Ag(111) with an exposure of 6400 L at room temperature.

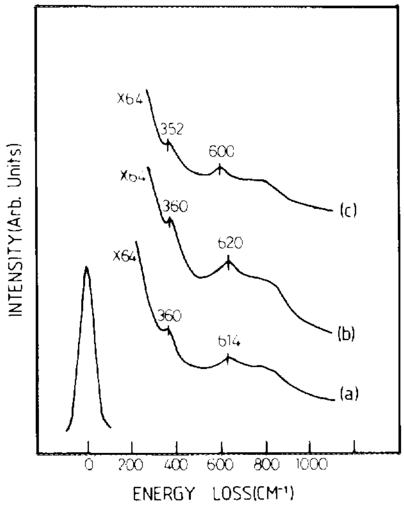

FIG. 4. HREEL spectra for oxygen adsorbed on Ag(111)/Cl-{a}: (a) after an exposure of 160 L O_2 at 170 K, (b) after an exposure of 480 L O_2 at 170 K, and (c) warming to room temperature from (b).

The TD spectrum allows us to estimate that on this surface the uptake of molecular oxygen is about 17% of that of atomic oxygen, which also indicates of the amount of defects present on our "nominal" (111) surface.

To study the effect of Cl on oxygen adsorption on Ag(111), we did experiments of oxygen adsorption on Ag(111) with preadsorptions of Cl to different stages or regimes. In a previous report (*8*) we analyzed earlier works on Cl adsorption on Ag(111) and, following an observation by Bowker and Waugh (*28*), showed that previous results can be brought into agreement in a consistent framework if one views Cl adsorption on Ag(111) as falling into three regimes: (a) low exposures of Cl produce a ($\sqrt{3} \times \sqrt{3}$)R30 overlayer pattern, the sample in this regime is denoted here as Ag(111)/Cl-{a}; (b) higher exposures to Cl give an epitaxial layer of AgCl(111) on Ag(111), denoted here by Ag(111)/Cl-{b} (this regime requires a defect-free starting surface); and (c) even higher exposures to Cl result in a surface which is a mixture of small crystallites of AgCl(111) and Ag(111), denoted here as Ag(111)/Cl-{c}.

The HREEL spectra of oxygen adsorption on Ag(111)/Cl-{a} at ≈170 K are shown in Fig. 4. The result, that both atomic and molecular oxygen species exist on the surface of Ag(111)/Cl-{a}, is similar to that of oxygen adsorption on Ag(111). It shows that in regime (a), Cl coadsorption has little effect on oxygen adsorption. Our Ag surface had too many defects and could not give a Ag(111)/Cl-{b} regime, and we are unable to report on the oxygen adsorption in this regime.

Figure 5 gives the HREEL spectra of oxygen adsorption on Ag(111)/Cl-{c}. In contrast to the Ag(111)/Cl-{a} regime, one finds a dramatic change in the surface oxygen species. Only molecular oxygen species exists on this surface at ≈170 K and room temperature regardless of the oxygen exposures. A comparison with Fig. 1 also shows that the amount of surface molecular oxygen species adsorbed on the surface is larger. This shows that when Cl is adsorbed to give regime (c), Cl adsorption has a pro-

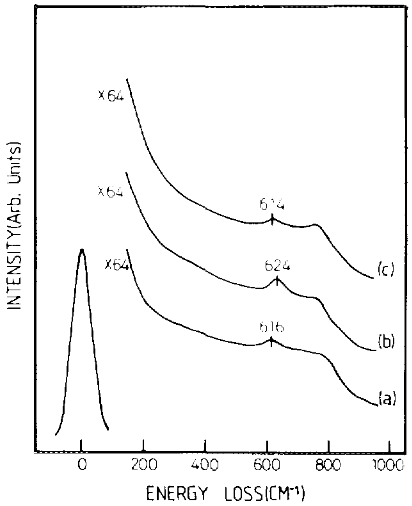

FIG. 5. HREEL spectra for oxygen adsorbed on Ag(111)/Cl-{c}: (a) after an exposure of 160 L O_2 at 170 K, (b) after an exposure of 480 L O_2 at 170 K, and (c) warming to room temperature from (b).

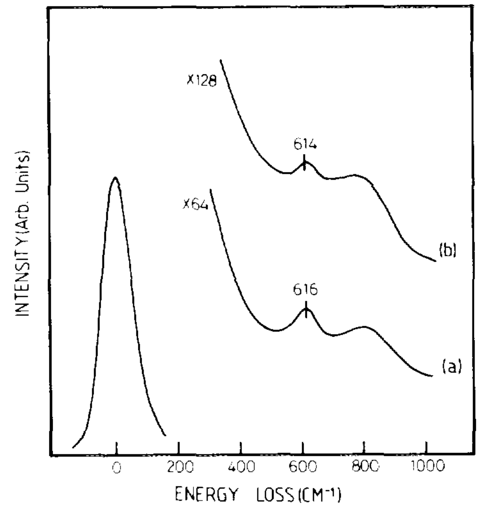

FIG. 6. HREEL spectra for oxygen adsorbed on Cl-modified Ag(111): (a) after an exposure of 480 L O_2 at 170 K and (b) warming to room temperature.

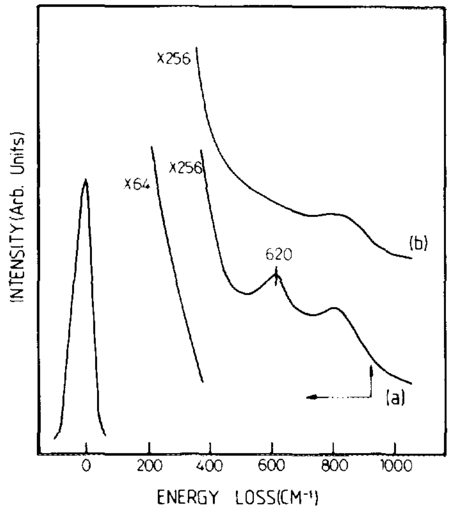

FIG. 7. HREEL spectra for oxygen adsorbed on Cl-modified Ag(111): (a) after an exposure of 1600 L O_2 at room temperature and (b) heating to 400 K.

found effect on oxygen adsorption on Ag(111).

In the next figure, we show that the alteration of oxygen adsorption by Cl in regime (c) is effective regardless of whether the Cl is present or removed. The Ag(111) sample which had been exposed to Cl to regime (c) was heated to 673 K to remove Cl, but was not annealed by heating to higher temperatures. We denote the Ag(111) sample with the above-described treatments as "Cl-modified Ag(111)." Later AES analysis confirmed the absence of Cl. We estimate that Cl left on this surface amounted to less than 1% of the surface. Figure 6 is the HREEL spectra of oxygen adsorption at ≈170 K on Cl-modified Ag(111). This is similar to the spectrum from Ag(111)/Cl-{c} and is different from those of Ag(111) and Ag(111)/Cl-{a}. Only the molecular oxygen species is present on this surface.

Figure 7 shows the HREEL spectra of oxygen adsorption on Cl-modified Ag(111) at room temperature. At this higher adsorption temperature, it is also the case that only the surface molecular oxygen species is produced. Here, the oxygen exposure is 1600 L and is four times less than that used (6400 L) on clean Ag(111), and implies that the sticking probability on this surface is increased. After the sample was heated to 400 K, the molecular oxygen desorbed (Fig. 7b). Figure 8 presents the TD spectra of oxygen adsorption on Cl-modified Ag(111) under the same adsorption conditions as in Fig. 7. A desorption peak at about 380 K indicates the presence of molecular oxygen. There is a temperature shift of about 10 K upward with an increase in the exposure of oxygen (Figs. 8a and 8b). This is likely due to the lateral interaction of adsorbates on the surface (*29*). A comparison of

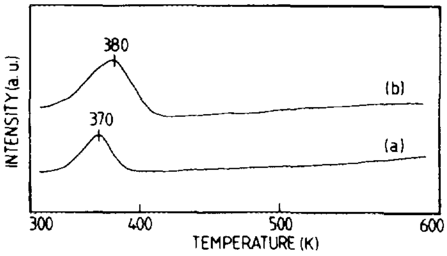

FIG. 8. TD spectra of oxygen on Cl-modified Ag(111): (a) after an exposure of 2400 L O_2 at room temperature and (b) after an exposure of 4800 L O_2 at room temperature.

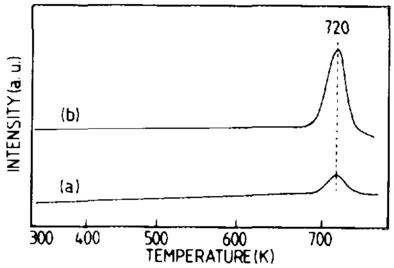

FIG. 9. TD spectra for subsurface oxygen in (a) Ag(111) and (b) Cl-modified Ag(111). The oxygen adsorption conditions are as follows: 4800 L oxygen adsorption at room temperature and evacuation by heating to 600 K; eight cycles in total are carried out.

the peak areas in Figs. 3 and 8 allows us to estimate that the total surface oxygen uptake on Cl-modified Ag(111) is about 35% of that on clean Ag(111).

Backx *et al.* (*30*) have studied subsurface oxygen in Ag(111) with TPD and isotope exchange techniques. They exposed a freshly sputter-cleaned Ag(110) surface (free of subsurface oxygen) to an 800-L oxygen dose at room temperature and heated the sample to above 585 K. With six more cycles of the same treatments, they detected a desorption peak at 725 K and assigned it to subsurface oxygen desorption. Rovida *et al.* (*31*) found that subsurface oxygen in Ag(111) desorbs at 780 K. With eight runs of the treatment of 4700-L oxygen adsorption and evacuation by heating to 600 K, we detected, on clean Ag(111), the subsurface oxygen desorption peak centered at 720 K (Fig. 9a). The subsurface oxygen desorption peak at 720 K was also present on Cl-modified Ag(111). We note that the area of the subsurface oxygen desorption peak on Cl-modified Ag(111) is several times larger than that on clean Ag(111).

DISCUSSION

We summarize our results here for discussion. Cl adsorption on Ag(111) in regime (a) does not severely perturb oxygen coadsorption. Cl adsorption on Ag(111) in regime (c) changes the form of oxygen adsorption from an atomic form to a molecular form for temperatures below 400 K. This result is less striking in our work because our starting Cl-free surface has some defects and already shows some molecular oxygen adsorption. But we can point to works from defect-free Ag(111) surfaces (*1*, *2*), and unpublished data on our Ag(111) before the creation of defects via Cl adsorption, which show that above 170 K only atomic oxygen is present and suggest that the result would be more striking if we had started with a defect-free surface. In addition, Cl adsorption on Ag(111) in regime (c) decreases the total amount of surface oxygen adsorbed, increases the sticking probability for oxygen adsorption and it increases the amount of subsurface oxygen. Cl alteration of the adsorption behavior on Ag is still present even after the removal of Cl.

We first consider the increased sticking probability of oxygen and argue that this is due to defect sites. We then discuss the presence of a stable molecular oxygen species and argue that this is from adsorption on surface defects. We show that this is a distinct type of defect and we introduce the term "Type-B defect" for it. We also point out that an increase in the amount of subsurface oxygen is consistent with the presence of Type-B defects. Thus, all three effects have in common the feature of defects. We summarize data in a previous report (*8*) that showed that an effect of Cl adsorption is the creation of defects (including Type B). This is circumstantial evidence that Cl adsorption affects oxygen adsorption via the creation of defects. However, when one also considers that Cl alteration of the adsorption behavior on Ag is still present even after the removal of Cl, then we have a good case.

The sticking probability of oxygen on Ag(111) is very small (about 5×10^{-6}) and it needs a high exposure (10^5–10^7 L) of oxygen for adsorption on Ag(111) (*1*). We have not done any experiments to quantify the sticking probability and shall leave our statement that the sticking probability is increased after Cl treatment as a qualitative statement. We estimate this initial sticking probability of oxygen in this work at 10^{-3} to 10^{-2} from the exposures used. A review of the literature shows that one can associate an enhanced sticking probability with defects.

On Ag, the (110) surface, a more open surface than the (111) surface, with troughs, shows a higher sticking probability than the (111) surface (*1*). Engelhardt and Menzel (*22*) and Albers *et al.* (*32*) showed that the sticking probability is enhanced by roughening; Albers *et al.* (*32*) used ion sputtering of Ag(111) and Engelhardt and Menzel (*22*) used a misoriented and faceted Ag(111). Works on polycrystalline Ag surfaces (*33–37*) have shown a much higher sticking probability for oxygen as compared with defect-free Ag(111) surfaces. The Ag surfaces include a polycrystalline Ag foil used by Prabhakaran and Rao (*33*), a polycrystalline Ag wire used by Ekern and Czanderna (*34*) (these authors (*33*, *34*) did not discuss the sticking probability but we can deduce that it is high from the exposures used), a "cold-deposited" Ag film used by Otto and co-workers (*35*, *36*), and a thick Ag film used by Hall and King (*37*). Grant and Lambert (*23*), however, reported that Ar ion bombardment does not increase the sticking probability on Ag(111). This is possibly related to the time of bombardment as Albers *et al.* (*32*) showed increases in sticking probability with the times of bombardment. Based on the other surfaces with enhanced sticking probability, we suggest that the site requirement(s) on these defects is not stringent. We refer to these sites as simply defects. Roughly speaking, we associate these defects with atomic scale roughness.

We now turn to a discussion of the observation of a stable form of molecular oxygen. Our results are similar to the finding by Kilty *et al.* (*10*) that Cl adsorption enhances molecular oxygen and decreases atomic oxygen. We can view our results as an extension of that classic work with supported Ag catalysts in that the same phenomenon is now seen with a single-crystal sample. Also, we have shown that Cl action does not require its continuous presence. We first discuss the nature of the molecular oxygen species that is created by Cl action. We denote this species as O_2(stable). We show that our notion of its adsorption site is consistent with our hypothesis for the mechanism of Cl action.

Two reviews (*1*, *2*) of the literature on oxygen adsorption on Ag show that a stable (stable to room temperature) molecular oxygen species, O_2(stable), is an elusive species, and yet evidence for its presence are also well documented (*10*, *17*, *19*, *23*). Many studies (*1*, *2*, *20*, *21*) from surface science have characterized molecular oxygen species that only exist below ca. 200 K which are probably precursor states of adsorbed atomic oxygen, and have also shown that O_2(stable) does not exist. We note that the surfaces used in these works are defect-free surfaces. We assume that the molecular species seen in these surface science studies are different from O_2(stable) and use the thermal stability to distinguish them. Their vibrational features are roughly the same. We now compare these with surfaces that have reported a stable molecular oxygen species. In three cases where O_2 (stable) was observed (*10*, *17*, this work), the surfaces were modified by Cl. We have argued previously (*8*) that an action of Cl is the creation of defects. In another case (*19*) of a surface that showed O_2(stable), the surface was an electrolytic Ag surface. Much work from the field of surface enhanced Raman spectroscopy (*38*) have shown that the electrolytic Ag surface is a much roughened surface. Another case of the observation of O_2(stable), by Grant and Lambert (*23*, *24*), was when oxygen was adsorbed onto Ag(111) at room temperature under a high pressure (≈1 Torr). Grant and Lambert pointed out that the presence of this molecular oxygen species was linked to the presence of subsurface oxygen and have also indicated the likely formation of $Ag_2O(111)$ on their surface. We now suppose that subsurface oxygen implies surface defects; a review of the dissolution of oxygen into metals (*39*) suggests mechanisms that are consistent with this assumption. With this assumption, we find that the common feature in the works that have reported O_2 (stable) is the presence of defects.

This allows us to put forward the proposition that we associate O_2(stable) with adsorption on defect sites. A corollary from the relative thermal stability of the molecular oxygen species on flat sites and defect sites is that adsorption on defect sites is stronger. Below, we argue that the site requirement(s) on these defects is quite stringent, and we term these defects as "Type B-defects" to distinguish them. We shall, because of the lack of experimental characterization of the defect sites, leave as vague this notion of defect. We have suggested that the defects responsible for increased sticking probability are associated with atomic scale roughness. We believe Type-B defects are associated with a more severe disruption of the surface—many polycrystalline Ag surfaces that show enhanced sticking probability do not show the presence of O_2(stable). We give our view on Type-B sites after we summarize Cl adsorption on Ag.

In contrast to the common observation of increased sticking probability on polycrystalline Ag, and most deliberately roughened Ag(111), the reporting of O_2(stable) on polycrystalline Ag was infrequent. It was reported by Kilty *et al.* (*10*) using Ag supported on alumina prepared by impregnation with $AgNO_3$. The molecular oxygen reported by Kilty *et al.* (*10*) adsorbed via a slow and activated process and may be a different species from our O_2(stable); in the next paragraph we argue they are the same. However, Ag used by Prabhakaran and Rao (*33*) and Otto and co-workers (*35, 36*) which showed increased sticking probability did not show O_2(stable). Molecular oxygen on their surfaces desorbed by 230 K. Prabhakaran and Rao (*33*) used a high-purity polycrystalline Ag foil, and Otto and co-workers (*35, 36*) used a "cold-deposited" Ag film specifically prepared to give atomic scale roughness. Evans *et al.* (*40*), using XPS and UPS, did not detect any molecular oxygen on polycrystalline Ag in the temperature range 298–353 K, that is, O_2(stable) was not seen. Dean and Bowker (*41*) did not report any TPD peak in the region of the O_2(stable) peak from Ag supported on alumina; one might expect this form of Ag to be quite rough, but Dean and Bowker (*41*) argued that their surface is (111)-like from their measurement of a very low sticking probability for oxygen, and one might exclude this from the cases of rough Ag that did not show O_2(stable). In our laboratory, we found that an Ag(111) surface treated with 1500 eV Ar ion bombardment for 20 min did not show an increase in O_2(stable). We further note that an Ag(331) surface, which is a stepped surface, used by Marbrow and Lambert (*42*) did not show stable molecular oxygen adsorption either.

There are works that have carried out oxygen adsorption at temperatures that are too high to make any firm deduction about the presence or absence of O_2(stable), but that might be construed to have shown O_2(stable) if one allows some assuming. These works adsorbed oxygen in the temperature range 373–473 K (for comparison, our O_2(stable) desorption peak temperature is 380 K and O_2(stable) desorbed by 400 K). In these works, a rough classification of oxygen adsorption was made (*1, 10, 43–45*) into: (1) a nonactivated adsorption as atomic oxygen, (2) an activated adsorption as molecular oxygen, and (3) an activated adsorption that leads to subsurface oxygen. Joyner and Roberts (*45*) studied this by XPS and isothermal adsorption at 473 K on polycrystalline Ag. They reported that the molecular oxygen species appeared only after prolonged exposure, 50 min under 5×10^{-3} Torr oxygen and which grew more distinct after 16 h, and after the appearance of subsurface oxygen. This may be a different molecular oxygen species from O_2(stable). We argue they are the same. There are two points of difference: our adsorption of O_2 (stable) is not activated and was relatively rapid, and it was desorbed by 400 K. To resolve the first difference with the molecular oxygen absorbed via an activated adsorption, we argue that the activation energy is not an activation energy of adsorption (this is a nondissociative adsorption) but the activation energy of a slow process that creates adsorption sites (Type-B defects) on which adsorbed oxygen exists in molecular form. Czanderna (*44*) has suggested that this process is the formation of Ag_2O. This is consistent with the induction period before the appearance of molecular oxygen seen by Joyner and Roberts (*45*). The difference in temperature could be due to differences in placement of the thermocouple point which can lead to differences of 50–100 K. In another case, Kagawa *et al.* (*46*), working with Ag powder, deduced molecular oxygen from the statistics of isotopic species. This was seen in the leading edge of a thermal desorption peak, in the temperature range 453–500 K, which is ca. 70 K higher than our O_2 (stable). Their adsorption temperature was 453 K. We again assume this molecular oxygen is the same as our O_2(stable). Kagawa *et al.* (*46*) reported that their Ag powder was pretreated and showed subsurface oxygen. One should note the similarity in the treatment conditions needed for the appearance of molecular oxygen in the above works and those Grant and Lambert (*23*, *24*) needed to detect O_2(stable) on Ag(111).

A valuable clue about Type-B defects may be in Ekern and Czanderna (*34*). Two desorption peaks, called α and β, were seen from a polycrystalline Ag wire. The α peak temperature was 460 K and the β peak temperature was 650 K. By comparison, our O_2(stable) peak temperature is 380 K and our atomic oxygen peak is 520 K. Ekern and Czanderna (*34*) assigned their β peak to atomic oxygen and commented that its temperature is higher than on other Ag surfaces, powders and single crystals, where this temperature is in the range 500–550 K. If we agree with this assignment of the β peak to atomic oxygen, then we could assume that their α peak is the same as our O_2(stable) peak. Ekern and Czanderna (*34*) worked mainly with an adsorption temperature of 435 K, but reported that the α peak was increased by adsorption at 300 to 410 K. A most interesting observation is that the α peak was not seen when their polycrystalline wire was thermally etched. This gave a surface that exposed "planes of both low and high Miller indices, with enhanced grain growth, grain boundary grooving and facet features." This implies, since there is only one desorption peak at 650 K, that the O_2(stable) adsorption site (Type-B defect) is not associated with grain boundary (between different planes) grooving and facet features. Additionally, if one assumes that the α peak is due to O_2(stable), then one can add that the adsorption sites of O_2(stable) are destroyed by a thermal etch, that is, heating in air at 1000 K for 12 h. There is a conflict with the works discussed in the previous paragraph that we cannot resolve but should point out: the thermal etch is apparently similar to the pretreatments that resulted in the observation of a molecular oxygen species. Perhaps the difference is in the temperature; those pretreatments were done at lower temperatures, 300–500 K, whereas the thermal etch by Ekern and Czanderna (*34*) was carried at 1000 K, which may cause annealing although it was described as etching.

We believe the above three paragraphs show that the site requirements on Type B defects are stringent. Many Ag surfaces with some form of roughness do not show O_2(stable) and those that do seem to first require some kind of treating. We next describe data (*8*) on Cl adsorption on Ag(111) and lead to our view about Type-B defects. We also consider other treatment conditions that create Type-B defects.

A model for Cl adsorption on Ag(111) for the regime Ag(111)/Cl-{c} and evidence that

Cl adsorption creates defect sites have been reported (*8*). This is a summary. AES shows an Ag(1) state besides the Ag(0) state which suggests that the AES signal is a convolution of a metallic Ag signal and an AgCl signal. Likewise, UPS and LEED data can be deconvoluted into signals from metallic Ag and AgCl. HREELS data showed a peak assignable to AgCl surface phonons. These prove the existence of AgCl. Two other details, revealed by HREELS, LEED, and ISS, are the presence of Ag defect sites and that the concentration of Cl on the Ag crystallites is much less than full coverage. These support a model of the structure of Ag(111)/Cl-{c} as a surface containing small Ag and AgCl crystallites. The observation by ISS that the surface concentration of Cl on the topmost surface layer of Ag(111) is far less than one monolayer in regime Ag(111)/Cl-{c} implies a facile dissolution of Cl into the bulk. This may be an important effect that "uncovers" Ag atoms to allow oxygen adsorption, but concerning our discussion here the important clue is the existence for a facile path for Cl dissolution.

We assume that the creation of defects (believed to include both atomic scale roughness and Type-B defects, but here we only consider Type-B defects) is concurrent with the appearance of AgCl crystallites. We also assume the concurrence of the opening of a pathway for a facile dissolution of Cl and, as we also argue from the increase in subsurface oxygen, of oxygen which suggests a severe disruption of the surface. We are, thus, inclined to believe that AgCl formation creates defect Ag regions at the interface around these crystallites due to misfit with the Ag(111) substrate, that is, grain boundary defects are created (which are different from the grain boundary grooving between planes of different Miller indices in Ekern and Czanderna (*34*)). We associate these grain boundary defects with Type-B defects from this circumstantial evidence.

We had argued that the adsorption sites of O_2(stable) are Type-B defects, that is, the presence of O_2(stable) is synonymous with the existence of Type-B defects. Using this we can note some other ways to create Type-B defects. Grant and Lambert (*23*, *24*), and perhaps Kilty *et al.* (*10*), Czanderna (*43*, *44*), Joyner and Roberts (*45*), and Kagawa *et al.* (*46*), show that these defects are created when Ag was "worked-in" by oxygen adsorption for a period under a relatively high pressure (≈1 Torr) at 300–500 K. In these cases, a common feature is the presence of subsurface oxygen and an activated process or induction period which may be due to the formation of Ag_2O (*43*). However, a comparison of the relative amounts of O_2(stable) to atomic oxygen on these surfaces with our surface also suggests that the amount of Type-B defects were less. In another case, Bao *et al.* (*19*) observed O_2(stable) on an Ag surface treated by an electrolytic "cleaning" treatment in a nitrate solution. This surface was characterized as a defect surface by HREELS (*19*). A similar electrolytic process was shown by Bergman *et al.* (*47*) to give a surface with a "random distribution of nodules."

An electrochemical cell is not analogous to a gas-solid adsorption system: there is the possibility of charge transfer and Ag dissolution into the electrolyte in an electrochemical cell. However, we feel that the above report by Bao *et al.* (*19*) together with a report by Kamenski *et al.* (*48*) that Cl treatment of Ag via adsorption from a NaCl solution also promotes Ag for ethylene epoxidation are cues that work in the area of electrochemistry might be relevant. Kazan *et al.* (*49*) showed that Ag surfaces are made highly defective (pitted) after an electrochemical treatment that forms AgCl crystallites on the Ag electrode. In work on Cl adsorption on Ag(111) in an electrochemical cell, Zei (*50*) reported, from RHEED data, the observation of 3D AgCl crystallites and structural defects. Zei (*50*) suggested that there is much similarity in the adsorbate behavior in adsorption in his electrochemical cell and adsorption in gas–solid systems. The defects in these cases could be from a different cause. On the other hand, these cases could also be supporting evidence of our claim (*8*) that Cl adsorption (from the gas phase) creates defects.

We now argue that Cl adsorption affects the mode of oxygen adsorption via structural changes to the Ag surface. We had commented that Cl adsorption Ag(111) can be grouped into three regimes (*8*). The salient features of the two regimes relevant here are that Ag(111)/Cl-{a} is a regime where Cl adsorption is the normal chemisorption and Ag(111)/Cl-{c} is a regime of Ag and AgCl and the structural changes described above.

Figure 4 shows that in regime (a), the effect of Cl coadsorption on oxygen adsorption is not strong: it is not visible in our experiments. Since regime (a) may be thought of as a coadsorption of Cl and oxygen, this could suggest that Cl action on oxygen adsorption is not through an electronic effect. In other works (*51*, *52*) on Cl action on oxygen adsorption, this was interpreted as showing that Cl and oxygen exist as separate islands. In the next paragraph, we give our second argument that Cl action is not via an electronic effect.

Most workers in this field have taken the view that Cl modification of the Ag surface is via an "electronic effect" (*2*), probably because Cl is one of the most electronegative element. Kilty *et al.* (*10*) and Campbell (*6*) have considered a "selective poisoning of ensembles effect" action. In both these mechanisms, the continuous presence of Cl is required for its action. Figs. 6–8 show evidence that Cl action is still present even after the removal of Cl. This together with the evidence that Cl adsorption creates defects argue that Cl action is through "structural effects." Later analysis of the surfaces in Figs. 6–8 showed that the Cl-modified surface after removal of Cl was roughened. The work function of the modified surface after removal of Cl, as measured by photoemission, had decreased by 0.3 eV. The Smoluchowski effect is the observation that, for chemically similar surfaces, rougher faces show lower work functions, and hence argues that the Cl-modified surface was roughened. Also, this surface could only show a high background in LEED and did not show any LEED pattern, again evidence of roughness. Thus, we conclude that the role of Cl adsorption in altering the mode of oxygen adsorption is through the creation of Type-B defects. Molecular oxygen is stable on these sites to 400 K.

An additional effect of Cl adsorption which we also associate with Type-B defects is increased subsurface oxygen. A consistent view is that the Type-B defects open a route for the easy penetration of surface atomic oxygen into the subsurface and the bulk. If there is no kinetic barrier to dissolution and it is supposed that oxygen atoms fit snugly in the interstices of the Ag lattice, and Rehren *et al.* (*53*) have argued that a good fit is the case, then there should be a concentration gradient of oxygen into the bulk according to thermodynamics; this would explain the very (undetectable in our case) small amount of atomic oxygen on the surface. A corroborating work is Joyner and Roberts (*45*), who reported that surface atomic oxygen was a transient species which was not seen after the appearance of subsurface oxygen and surface molecular oxygen.

One other effect of Cl adsorption is a decrease in the surface oxygen concentration. In our model, this is due to the formation of AgCl crystallites. We assume that oxygen does not adsorb on AgCl.

CONCLUSION

Cl adsorption affects oxygen adsorption on Ag(111) through defects (including Type-B defects) created with the formation of AgCl in regime (c) of Cl adsorption. These have three functions in oxygen adsorption: (1) increase the adsorption rate of oxygen, (2) Type-B defects stabilize surface molecular oxygen, and (3) Type-B defects give a facile route for surface atomic oxygen to diffuse into the subsurface to become subsurface oxygen. The formation of AgCl results in a decrease in the amount of oxygen on the surface. The action of Cl is via structural changes rather than an electronic ligand effect or an ensemble effect.

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