

Chlorination of Silver Dosed with Potassium and Barium in Presence of Oxygen: An X-Ray Photoelectron Spectroscopy Study¹

M. AYYOUB AND M. S. HEGDE²

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

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XPS studies show that the presence of chemisorbed chlorine stabilizes and also enhances molecular dioxygen species on Ag surfaces dosed with either K or Ba. The surface atomic oxygen is found to become depleted on chlorination. The variation in the nature of surface species with respect to temperature shows chlorine-induced diffusion of atomic oxygen into the subsurface region at 300 K. For coverages of potassium up to 8×10^{14} atoms/cm², preferential chlorination of Ag occurs while at higher potassium coverages, KCl formation is distinctly observed on the surface. In the case of barium, two types of adsorbed chlorine species, Cl(α) and Cl(β), associated with Ag and Ba, respectively, are clearly seen even at low barium coverages. This is believed to be due to the higher valence occupation of barium compared to potassium. The Cl(α) species associated with Ag is found to occupy a preferred site on both K- and Ba-dosed surfaces, involving chemisorptive replacement of O(α) to the subsurface region. © 1986 Academic Press, Inc.

INTRODUCTION

Alkali metal atoms and chlorine are believed to enhance the selectivity of the silver catalyst used in the epoxidation of ethylene (1, 2). Oxides of alkali metals such as K₂O, compounds of barium and chlorides such as KCl are routinely added to silver catalysts for the selective oxidation of ethylene to ethylene oxide (2). Surface sensitive techniques like X-ray photoelectron spectroscopy and UV photoelectron spectroscopy can be fruitfully employed to understand the role of such additives. In our recent XPS study of oxygen adsorbed on potassium- and cesium-covered Ag surfaces, three different types of oxygen species, viz., oxide oxygen (O²⁻), dissociatively chemisorbed atomic oxygen (O^{x-}, $x < 2$) and molecular dioxygen (O₂ ^{δ -}, $\delta < 2$) have been isolated (3). It was of interest to examine by XPS if the adsorption of chlorine could effect a change in the oxygen

adsorption behavior on the alkali-covered Ag surface and to see if molecular dioxygen species could be stabilized on the surface at room temperature. Kitson and Lambert (4) have reported in their thermal desorption studies that preadsorbed chlorine blocks the surface to chemisorbed atomic oxygen on a potassium-dosed Ag(100) surface. Studies of chlorine on the Ag(111) surface by temperature-programmed desorption have shown the presence of chemisorbed chlorine and AgCl (5). In this laboratory, Kamath *et al.* (6) have studied the effect of chlorine on the adsorption behavior of oxygen on Cu and Ag. It has been shown that atomic oxygen adsorption is suppressed on chlorine-presorbed surfaces and only molecular dioxygen is seen at 80 K. Here we report XPS studies of the adsorption of chlorine on potassium- or barium-dosed Ag surfaces saturated with oxygen. We have also studied adsorption of oxygen on chlorine-presorbed Ag surfaces dosed with potassium or barium. Changes in the nature of adsorbed species and their surface concentrations as a function of temperature have been studied.

¹ Contribution No. 266 from the Solid State and Structural Chemistry Unit.

² To whom correspondence should be addressed.

EXPERIMENTAL

MgK α X-ray excited photoelectron spectra were recorded in an ESCA 3 Mark II spectrometer (V.G. Scientific Ltd., U.K.) equipped with a preparation chamber. Polycrystalline Ag in the form of a foil (0.5 mm thick) was cleaned by repeated heating in oxygen (850 K, 10⁻⁴ Torr) and Ar ion etching. The spectrometer was operated under high resolution (20 eV pass energy) for the XPS study and the FWHM of Ag(3d_{5/2}) was 1.1 eV. Binding energies reported here are with reference to the kinetic energy of Ag(3d_{5/2}) at 885.1 eV.

Potassium was dosed on to the surface from a zeolite source while barium was deposited from a Ba-getter. The base vacuum in the spectrometer and preparation chambers was of the order of 5 × 10⁻¹⁰ Torr. The gases were exposed from precision leak valves in the preparation chamber at a maximum pressure of 10⁻⁶ Torr in the case of Cl₂ and at 10⁻⁵ Torr for O₂. The purity of O₂ and Cl₂ used in the experiments was checked in the preparation chamber using a Q-7 quadrupole mass spectrometer (V.G. Scientific Ltd.). There were no detectable impurities of H₂O, HCl, or CO when chlorine was leaked at 10⁻⁸ Torr. Gas exposures have been expressed in terms of Langmuirs (1 L = 10⁻⁶ Torr · s). The surface concentrations of adsorbates have been estimated by following the method of Carley and Roberts (7) using the photoionization cross sections from Scofield (8). The surface concentrations have been calculated assuming single film adsorption and have been expressed in terms of atoms per square centimeter (σ) as the silver sample used being polycrystalline, the surface atom density is ill-defined.

RESULTS

In each of these experiments, the silver surface was first dosed with alkali. It was then exposed to oxygen and chlorine. The order in which these gases are exposed is mentioned in each of the cases. The O(1s),

Cl(2p), and metal core levels were monitored at each stage.

Potassium-dosed Ag

The nature of adsorbed oxygen seen on potassium-covered Ag has already been reported (3). Figure 1a shows the O(1s) and Cl(2p) spectra before and after chlorine exposure to the oxygen-presorbed surface. The surface concentration of potassium in this experiment is 8.2 × 10¹⁴ atoms/cm². Before chlorine adsorption, the O(1s) region shows peaks around 529, 531, and 533 eV attributable to oxygen species, O²⁻, O^{x-}, and O₂^{δ-}, respectively ($\delta, x < 2$) (3). After chlorine exposure (1000 L), the lower binding energy peaks (designated by O(α) and O(β)) occurring at 529 and 531 eV are greatly suppressed and the peak at 533 eV becomes distinct and prominent. The Cl(2p) region shows a clear 2p_{3/2,1/2} doublet at 198.2 and 199.7 eV, respectively.

We were interested in examining whether significant atomic oxygen adsorption can be effected after exposure to small dosages of chlorine. In Fig. 1b we have shown the O(1s) and Cl(2p) spectra observed when Cl₂ is adsorbed prior to oxygen. The spectra after 1 L Cl₂ exposure to potassium-covered Ag are shown. The Cl(2p) region shows a simple Cl(2p_{3/2,1/2}) doublet with the binding energy same as in Fig. 1a. After 1000 L O₂ exposure to this surface, only a small O(1s) peak is observed around 533 eV. The Cl(2p) binding energy remains unaltered after oxygen adsorption. However, there is some decrease in the Cl(2p) intensity, as can be seen from Fig. 1b.

Figure 2 shows the K(2p), O(1s), and Cl(2p) spectra for different coverages of potassium recorded after chlorine exposure (1000 L) to the oxygen-saturated surface. Curve A shows the Cl(2p) spectrum after chlorine exposure (1000 L) to the clean Ag surface at 300 K without any potassium coverage. The Cl(2p_{3/2}) binding energy is observed at 198.0 eV. The surface concentration of this chlorine on the clean Ag surface is 5 × 10¹⁴ atoms/cm².

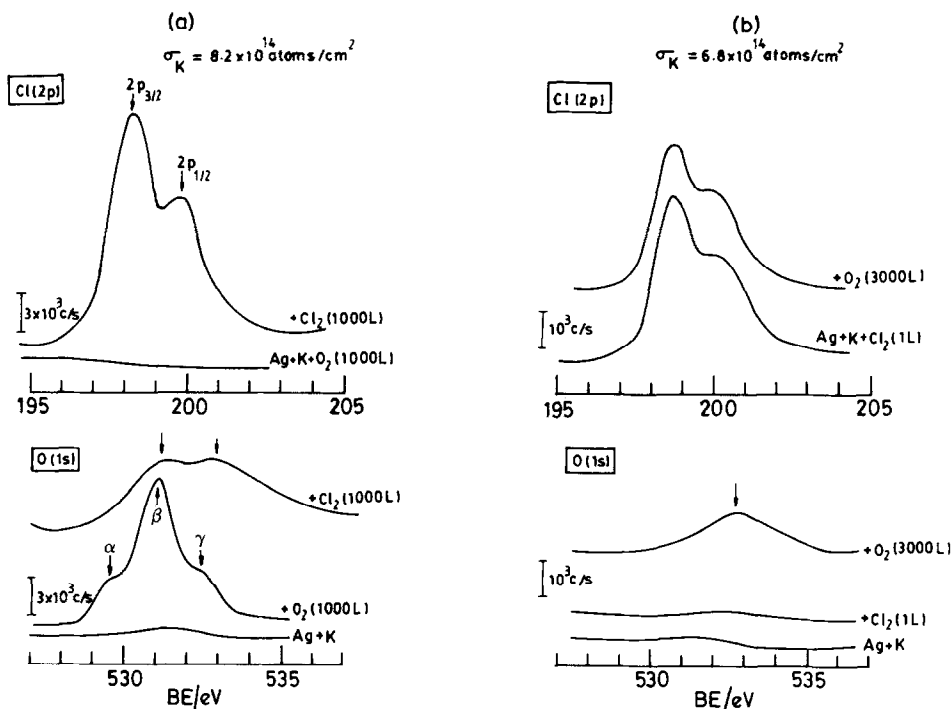


FIG. 1. Cl(2p) and O(1s) spectra on potassium-dosed Ag after (a) O₂ dosage followed by Cl₂ dosage, (b) Cl₂ dosage followed by O₂ dosage.

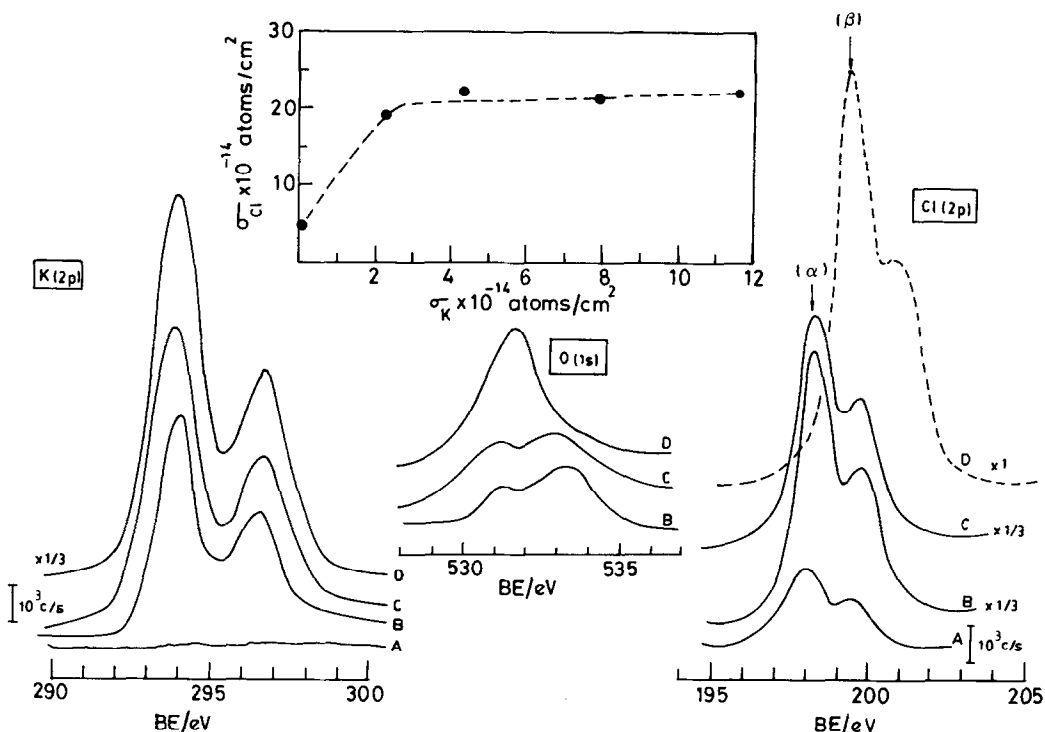


FIG. 2. K(2p), O(1s), and Cl(2p) spectra on Ag + K + O₂ + Cl₂ for various potassium coverages at 300 K. The K concentrations are (A) zero, (B) 4.3×10^{14} , (C) 6.4×10^{14} , and (D) $24.4 \times 10^{14} \text{ atoms/cm}^2$ (O₂ and Cl₂ exposures: 1000 L). Inset shows the variation in chlorine concentration with the K concentration after 1000 L Cl₂ exposure to Ag + K + O₂.

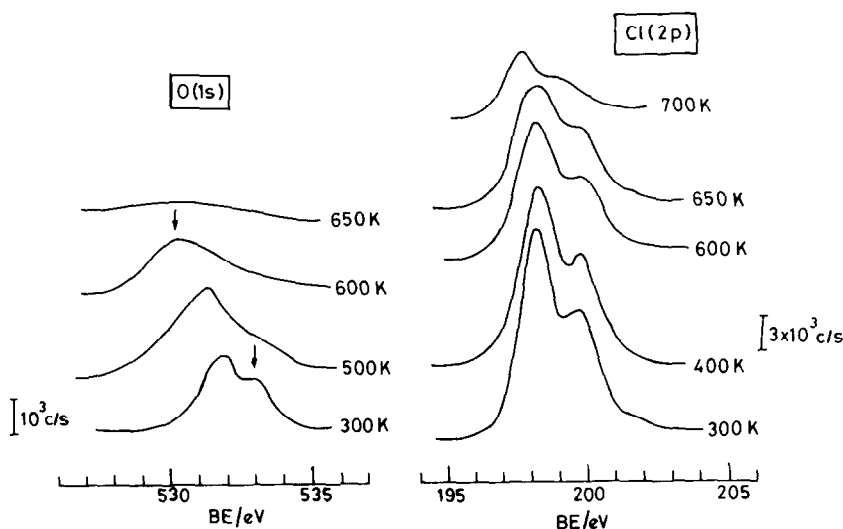


FIG. 3. Variation in the nature of O(1s) and Cl(2p) spectra with temperature on Ag + K + O₂ + Cl₂ (O₂ and Cl₂ exposures: 1000 L; $\sigma_K \approx 5 \times 10^{14}$ atoms/cm² at 300 K).

The saturated chlorine coverages on various predosed concentrations of potassium were studied. For this, after each potassium dosage, oxygen was exposed (1000 L) and the surface was checked to see that no pickup of chlorine has taken place. Chlorine (1000 L) was then exposed to this surface. In Fig. 2 are shown the K(2p) and the corresponding O(1s) and Cl(2p) spectra (curves B, C, and D). It is evident from these curves that saturation coverage of chlorine can be significantly enhanced on the potassium-dosed surface. The Cl(2p_{3/2}) binding energy observed at 198.2 eV is quite close to that observed in the presence of potassium up to 8×10^{14} atoms/cm². For very high potassium coverages, on the contrary, there is a shift of Cl(2p_{3/2}) to higher binding energy (199.4 eV) as can be seen in curve D ($\sigma_K > 1.5 \times 10^{15}$ atoms/cm²). In the O(1s) region, the 533 eV O(1s) peak remains practically the same for various potassium coverages. Some decrease in intensity of this peak is noticed only for very high potassium coverages. The intensity of O(α) (529.5 eV) is totally suppressed for all values of σ_K . The intensity of O(β) after suppression, however, increases with increase in σ_K as is clear from Fig. 2.

The saturated chlorine concentration has been estimated for different potassium coverages. The inset in Fig. 2 shows σ_{Cl} as a function of potassium coverage, σ_K .

In Fig. 3, the variation in the O(1s) and

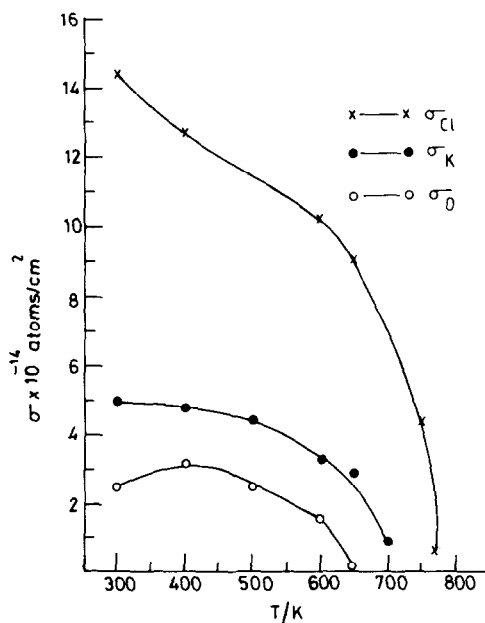


FIG. 4. Variation in the surface concentrations of Cl, K, and O with temperature on Ag + K + O₂ + Cl₂ (O₂ and Cl₂ exposures: 1000 L).

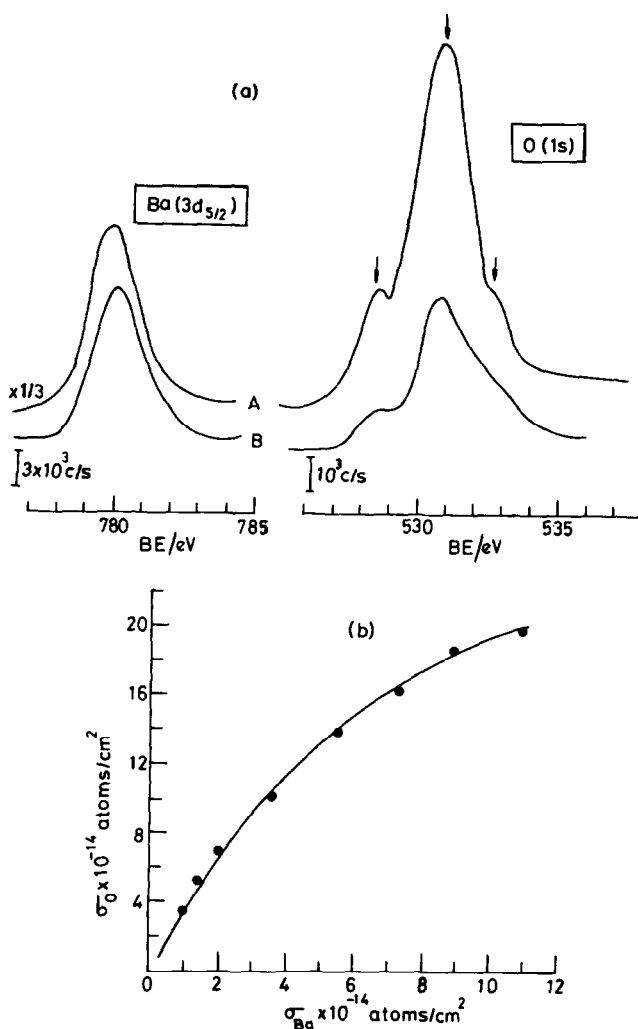


FIG. 5. (a) Ba(3d_{5/2}) and O(1s) spectra on barium-dosed Ag saturated with O₂ for (A) $\sigma_{\text{Ba}} = 5.4 \times 10^{14}$ and (B) $\sigma_{\text{Ba}} = 1.4 \times 10^{14}$ atoms/cm². (b) Variation in saturated O₂ coverages as a function of barium coverage.

Cl(2p) spectra as a function of temperature is shown. On heating, there is a major decrease in the emissions at 533 and 531 eV in the O(1s) region. Further, a peak around 530 eV begins to appear at 500 K. This peak becomes quite prominent at 600 K. At 650 K, all the oxygen is found to desorb. The adsorbed chlorine also decreases in intensity. The Cl(2p) binding energy also shows some decrease at higher temperatures. At 700 K, the Cl(2p_{3/2}) shifts by about 0.5 eV to lower binding energy. The variation in the surface concentrations of potassium, chlo-

rine, and oxygen with temperature is shown in Fig. 4 for a typical potassium coverage of 5×10^{14} atoms/cm².

Barium-dosed Ag

(a) *Oxygen on barium-dosed Ag.* Figure 5 shows typical O(1s) spectra observed on oxygen exposure to barium-covered silver for two different barium coverages at 300 K. A shoulder at 528.6 eV, an intense peak at 530.8 eV and another shoulder at 533 eV are clearly seen. Increase in the surface concentration of barium is found to result in

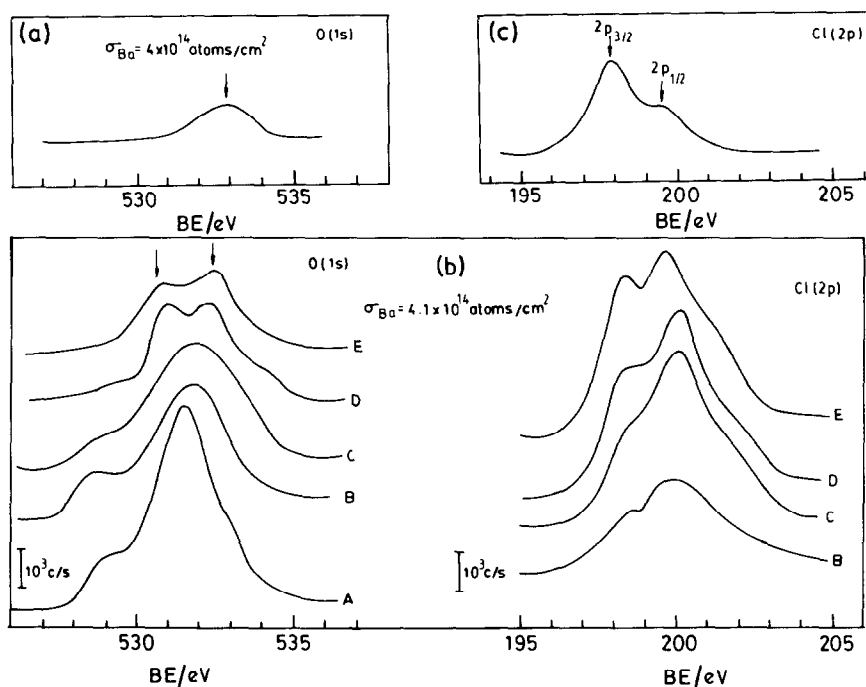


FIG. 6. (a) O(1s) spectrum on Ag + Ba + Cl₂(1 L) + O₂(3000 L). (b) O(1s) and Cl(2p) spectra on (A) Ag + Ba + O₂ (100 L) and after (B) 1 L, (C) 100 L, (D) 1000 L, and (E) 10⁴ L chlorine exposure. (c) Cl(2p) spectrum on Ag + Cl₂ (1000 L) at 300 K.

a selective increase in the intensity of the ~531 eV O(1s) peak after oxygen saturation, suggesting its association with barium. Also shown in Fig. 5 is the variation of the total saturated oxygen coverage with increase in σ_{Ba} . It is found that at smaller barium coverages, the oxygen-to-barium concentration ratio is significantly high. With increase in σ_{Ba} , the ratio decreases from about 4 to 2.0. The solid line in the plot is a fit to the equation

$$\sigma_O = a[1 - \exp(-b\sigma_{Ba})],$$

where a and b are empirical constants (3). The value of the product “ ab ” has been shown to give the oxygen uptake coefficient σ_O/σ_{Ba} for low Ba coverages (3). The value of ab in the case of barium is 3.80 while it has lower values for potassium- and cesium-covered Ag surfaces, viz., 2.49 and 3.12, respectively (3).

(b) *Chlorine on barium-dosed Ag.* The barium-dosed Ag surface was given a small

exposure of chlorine (1 L). The surface was then dosed with excess of O₂ (3000 L) and the O(1s) spectrum seen after this exposure is shown in Fig. 6a. It is clear that a single O(1s) peak is observed with binding energy at 533 eV. The effect of chlorine on pre-adsorbed oxygen on the barium-covered Ag surface is shown in Fig. 6b as a function of chlorine dosage. After only 1 L Cl₂ exposure, the shoulder at 529 eV and the sharp peak at ~531 eV are considerably reduced in intensity, while at the same time a broad peak centered around 533 eV is clearly observed. For higher doses of chlorine, the peak at 529 eV is totally suppressed and a distinct peak emerges at 533 eV as can be seen in curve E (after 10⁴ L Cl₂ exposure). The corresponding Cl(2p) signals with increasing chlorine exposure are also shown in Fig. 6b. The Cl(2p) spectrum after chlorine adsorption on clean silver is shown in Fig. 6c. By comparing the Cl(2p) spectra on clean and barium-dosed Ag, one can clearly

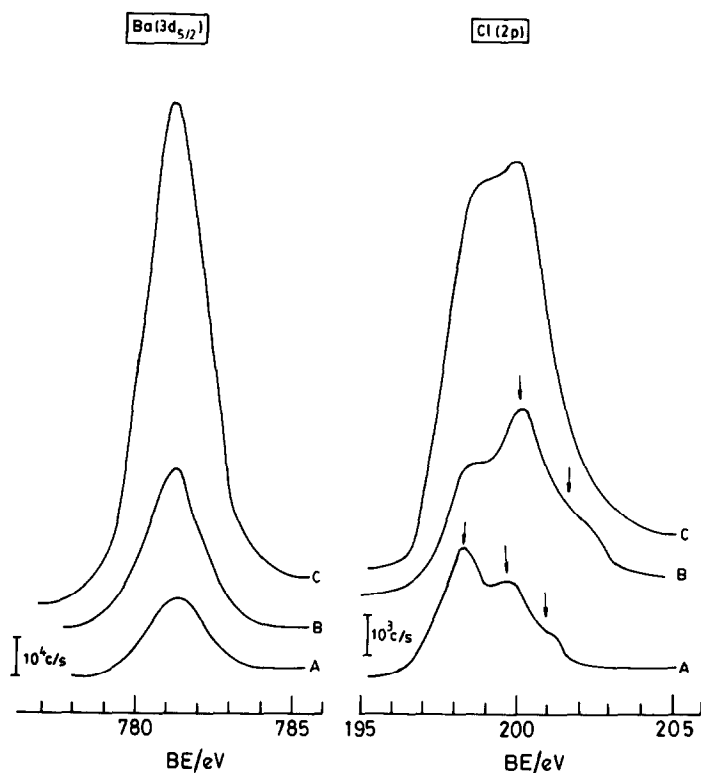


FIG. 7. Ba(3d_{5/2}) and Cl(2p) spectra on Ag + Ba + O₂ + Cl₂ for various barium coverages ($\sigma_{\text{Ba}} = 2 \times 10^{14}$, 3.5×10^{14} , and 15×10^{14} atoms/cm² for A, B, and C, respectively; O₂ and Cl₂ exposures: 1000 L).

see the presence of more than one type of Cl(ad) species on the barium-covered surface. To understand the nature of these peaks, the variation of Cl(2p) with barium coverage was studied. The results are shown in Fig. 7. For smaller barium coverages ($\sigma_{\text{Ba}} = 4 \times 10^{14}$ atoms/cm²; curve A), the main Cl(2p) binding energy is similar to that on clean silver. As the barium coverage is increased the total intensity of adsorbed chlorine also increases, and a preferential growth of a high-binding-energy Cl(2p) peak is observed. In Fig. 8a the curves A and B show Cl(2p) spectra after 10 L and 1000 L Cl₂ exposure to Ag + Ba + O₂ ($\sigma_{\text{Ba}} = 1.5 \times 10^{15}$ atoms/cm²). The difference between the two spectra (shown in the figure) clearly indicates the growth of a low-binding-energy Cl(2p) signal for higher doses of chlorine. In Fig. 8b, the Cl(2p) spectrum in the case of a different barium coverage ($\sigma_{\text{Ba}} = 4 \times 10^{14}$ atoms/cm²) has

been shown along with the curve-fitted resolved peaks into the (Cl2p_{3/2,1/2}) components. Two distinct Cl(2p) peaks are observed, one with a lower binding energy Cl(α) and another Cl(β) with a separation of about 1.7 eV. The relative growth of Cl(α) and Cl(β) peaks as a function of chlorine dosage is shown in Fig. 8c. It is clear that Cl(β) grows exponentially while Cl(α) increases linearly with logarithm of exposure.

On examining the effect of temperature, it was noticed that the intensity of Cl(α) started decreasing on heating and at 725 K, almost no Cl(α) was seen on the surface. However, the high binding energy Cl(β) was found to remain on the surface at this temperature. The decrease in the concentration of Cl(α) was accompanied by a corresponding increase in O(α) intensity. At 725 K, the peak at 529.5 eV was found to be very distinct and prominent. This selective replacement of Cl(α) with O(α) on the bar-

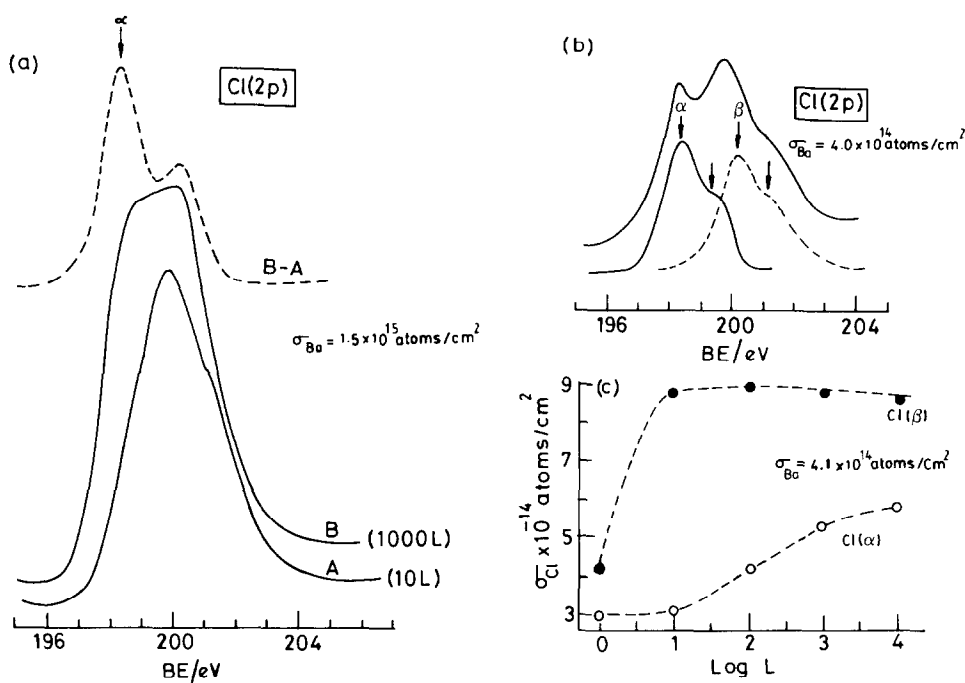


FIG. 8. (a) Cl(2*p*) spectra on Ag + Ba + O₂ after (A) 10 L and (B) 1000 L Cl₂ exposure at 300 K ($\sigma_{\text{Ba}} = 1.5 \times 10^{15}$ atoms/cm²). (b) Cl(2*p*) spectrum on Ag + Ba + O₂ + Cl₂ and the curve-fitted resolved 2*p*_{3/2,1/2} components of Cl(α) and Cl(β) ($\sigma_{\text{Ba}} = 4 \times 10^{14}$ atoms/cm²; O₂ and Cl₂ exposures: 1000 L). (c) Variation in surface concentrations of Cl(α) and Cl(β) with logarithm of Cl₂ exposure (in Langmuirs) on Ag + Ba + O₂ + Cl₂ ($\sigma_{\text{Ba}} = 4.1 \times 10^{14}$ atoms/cm²; O₂ and Cl₂ exposures: 1000 L).

ium-covered surface is very much analogous to the effect observed on the potassium-covered surface as described earlier. There was little change in the intensity of the Ba(3*d*_{5/2}) peak up to 725 K.

DISCUSSION

The presence of a weakly chemisorbed dioxygen species has been seen in earlier studies on alkali-promoted silver surfaces using XPS (3) and "thermal desorption spectra" (TDS) (9) techniques. The O(1*s*) feature at 533 eV has been attributed to adsorbed molecular dioxygen species (3, 10). In the present study, we notice that on adsorption of excess oxygen to the chlorine-adsorbed surface, only the 533-eV peak emerges (see Figs. 1b and 6a). Also, on examining the effect of chlorination of pre-adsorbed oxygen, we again find that the 533-eV peak becomes very prominent and

distinct (see Figs. 1a and 6b). This clearly suggests that the presence of chlorine induces a stabilization of molecular dioxygen at 300 K on both potassium- and barium-dosed surfaces. In their thermal desorption studies, Kitson and Lambert (4) found that alkali-induced dioxygen is hardly affected by chlorine adsorption either prior to or after oxygen adsorption on potassium-dosed Ag.

In addition to the stabilization of molecular oxygen, a pronounced decrease in surface concentration of chemisorbed oxygen is observed on chlorine exposure to both potassium- and barium-dosed surfaces. The lower binding energy oxygen, O(α), associated with Ag is totally suppressed. One possible reason is chlorine-induced diffusion of this oxygen into the subsurface region.

On clean Ag, adsorption of chlorine

results in a $\text{Cl}(2p_{3/2,1/2})$ doublet with binding energies at 198.0 and 199.5 eV, respectively. These values agree very well with those reported earlier for chemisorbed chlorine on $\text{Ag}(100)$ (11). The concentration of this adsorbed chlorine is found to be around 5×10^{14} atoms/cm². Earlier studies on chlorination of Ag single crystal surfaces by TDS and LEED have primarily shown the formation of chemisorbed atomic chlorine at 300 K (11–14). In a more recent study, Bowker and Waugh (5) have also arrived at a similar conclusion with the $\text{Ag}(111)$ plane.

On the potassium-covered surface, the surface concentration of adsorbed chlorine is found to be greatly increased, as is evident from Fig. 2. While the concentration of $\text{Cl}(\text{ad})$ on clean silver is 5×10^{14} atoms/cm², potassium coverage leads to an increase in the concentration to 2×10^{15} atoms/cm² upon saturation. On the potassium-dosed surface, the nature of $\text{Cl}(2p)$ spectra suggests that surface $\text{Cl}(\text{ad})$ is present as a single type of chemisorbed species and is preferentially associated with Ag for coverages of potassium even up to 8×10^{14} atoms/cm², as can be seen from the $\text{Cl}(2p_{3/2})$ peak at 198.2 eV. Furthermore, the saturated chlorine coverage is found to be independent of potassium dosage σ_K as can be seen from the inset in Fig. 2. This also suggests chlorine association with Ag. The higher binding energy $\text{Cl}(2p)$ peak observed at around 199 eV for very high potassium coverages ($\sigma_K \sim 1.5 \times 10^{15}$ atoms/cm²) could be attributed to surface KCl islands. These observations are indeed supported by TDS studies by Kitson and Lambert (4). For $\theta_K < 0.5$, a significant amount of AgCl desorption was found to occur in their study even for chlorine coverages as low as $\theta_{\text{Cl}} = 0.1$ and for $\theta_K > 0.5$, no AgCl desorption was observed, i.e., all the chlorine desorbed in the form of KCl. Also, $\text{Cl}(2p_{3/2})$ binding energy has indeed been observed at 199.1 eV for the analogous compound NaCl (15). Further, in our study, the adsorbed chlorine concentration is found to

be much higher than the potassium concentration (see Fig. 2, inset). This also supports the view that the surface chlorine is mostly associated with Ag for lower coverages of potassium.

It should be mentioned that the leveling-off of saturation chlorine coverages after 1000 L Cl_2 exposure observed in the inset of Fig. 2 is unlikely to be due to the limiting escape depth of XPS. The Cl and Ag atom radii in AgCl being 1.81 and 1.26 Å, we can take the Ag–Cl single layer thickness to be nearly 3 Å. The surface Cl concentration of 2×10^{15} atoms/cm² would be less than two layers in thickness (roughly taking 1.4×10^{15} atoms/cm² as a monolayer). This would mean that the thickness of these layers under study is in the range of 5–6 Å which is well within the maximum escape depth in Ag. Also for a typical potassium coverage of 3×10^{14} atoms/cm² with a corresponding σ_{Cl} of 2×10^{15} atoms/cm², the thickness of the total adlayer calculated from the exponential decrease in $\text{Ag}(3d_{5/2})$ signal as compared with that in the case of clean Ag surface is found to be 5.5 Å, taking the mean escape depth as 11.5 Å (16) at the $\text{Ag}(3d_{5/2})$ peak kinetic energy. This again suggests that the thickness of two to three monolayers of AgCl on the surface is within the sampling depth of XPS.

The study of the concentrations of the oxygen species on the surface with respect to temperature shows an interesting feature. With decrease in the intensity of $\text{Cl}(\alpha)$ at higher temperatures, a corresponding increase in the intensity of $\text{O}(\alpha)$ is observed. At 600 K, $\text{O}(\alpha)$ is found to be quite prominent on the potassium-dosed surface. A very similar effect is indeed observed on the barium-covered surface. $\text{Cl}(\alpha)$, in this case, desorbs at 725 K with simultaneous increase in $\text{O}(\alpha)$. This observation and the drastic decrease in the intensity of $\text{O}(\text{ad})$ observed on chlorination at 300 K together indicate that $\text{Cl}(\text{ad})$ induces surface to bulk diffusion of atomic oxygen. The saturation concentration of $\text{Cl}(\text{ad})$ is higher than that of presorbed oxygen which means that it is

not just a one-to-one chemisorptive replacement of O(α) by Cl(α) but the formation of a preferred Ag-Cl surface structure. Our results are in good agreement with LEED studies on the Ag(100)/K/O₂/Cl₂ system where a preferred C(2 × 2) structure has been observed. These observations, therefore, clearly suggest that Cl(α) associated with Ag tends to occupy a highly preferred site on both potassium- and barium-dosed surfaces involving a displacement of surface O(ad).

The decrease in surface Cl(ad) concentration from Ag + K + O₂ + Cl₂ (Fig. 4) shows a trend marked by a transition at about 650 K. Above this temperature, the decrease in Cl(ad) is very drastic and signifies desorption of AgCl. This is in conformity with TDS studies on Ag(111) + Cl (5) where desorption of AgCl has been seen above 600 K, with the peak temperature at 670 K. Below 650 K, we notice a decrease in surface Cl concentration by 5×10^{14} atoms/cm². In this temperature range, there is also the enrichment of surface O(α). This decrease in σ_{Cl} below 600 K, we think, is due to subsurface dissolution of Cl.

The decrease observed in the Cl(α) binding energy on heating is possibly due to greater ionicity in the metal-Cl bond at higher temperatures. In this connection, it is significant to mention that on Ag(100), work function measurements (12) have indicated transformation of chemisorbed chlorine to AgCl at 430 K.

In the case of the barium-covered surface, one important difference noticed is that composite Cl(2*p*) peaks are observed attributable to Cl(ad) associated with both Ag as well as barium even for relatively low Ba coverages. This is clearly borne out from the curve-fitted resolved peaks showing Cl(α) and Cl(β) components. This is in contrast to the potassium-covered surface where a single sharp Cl(2*p*) associated with Ag is observed even up to $\sigma_{\text{K}} = 8 \times 10^{14}$ atoms/cm². From Figs. 6, 7, and 8, some of the obvious results are the following: the intensities of both the Cl(α) and Cl(β) peaks

are functions of chlorine dosage and the saturated intensities of Cl(α) and Cl(β) peaks are functions of barium dosage. With increase in σ_{Ba} , the increase in saturated intensity of Cl(β) is much more marked than that of Cl(α). Furthermore, the binding energy of Cl(α) matches well with that of Cl(2*p*_{3/2}) on Ag + Cl. Based on these observations, it is reasonable to assign Cl(α) and Cl(β) to adsorbed chlorine associated with Ag and barium, respectively. This assignment is also analogous to that in the case of O(ad) on Ag + Ba + O₂.

The presence of two Cl(ad) species on the barium-dosed surface at relatively low barium coverages is contrary to what is observed on the potassium-dosed surface at similar potassium coverages. It is well known that electron transfer from the alkali to the transition metal is responsible for the changes brought about in adsorption phenomena by alkali adatoms (17-19). By electron transfer, silver is thus expected to become enriched in valence electron density, thereby facilitating backtransfer to Cl(3*p*) in the chloridation process. Due to higher valence occupation in barium compared to potassium, one would expect sufficient charge density to remain on barium, even after electron transfer, to facilitate Ba-Cl

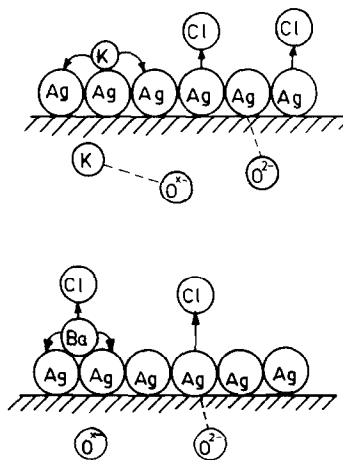


FIG. 9. Schematic diagram of electron transfer showing metal-chlorine interaction in Ag/K and Ag/Ba systems.

interaction. This is schematically shown in Fig. 9.

CONCLUSIONS

Characteristic Cl(2*p*) and O(1*s*) peaks are seen by XPS which are attributable to distinct adsorbed chlorine and oxygen species on potassium- and barium-dosed Ag surfaces.

(a) There is selective stabilization of molecular dioxygen species on both potassium- and barium-dosed Ag surfaces at 300 K in the presence of adsorbed chlorine. When chlorine is adsorbed prior to oxygen, only molecular dioxygen stabilizes on excess O₂ dosage.

(b) On chlorination, the intensity of pre-adsorbed oxygen on the surface is found to decrease appreciably. This could possibly be due to chlorine-induced diffusion of atomic oxygen into the subsurface region.

(c) For $\sigma_K < 8 \times 10^{14}$ atoms/cm², preferential chlorination of Ag takes place, as shown by a single Cl(2*p*) peak. For higher potassium coverages, a high-binding-energy Cl(2*p*) peak is seen due to adsorbed chlorine associated with potassium.

(d) In the presence of either potassium or barium, the saturation intensity of Cl(α) associated with Ag is considerably enhanced. The saturated coverage of Cl(ad) is independent of potassium coverage in Ag/K/O₂/Cl₂ system while it does increase with increase in barium concentration.

(e) On the barium-dosed surface, two characteristic Cl(ad) species, namely Cl(α) associated with Ag and Cl(β) associated with barium, are observed even for relatively low barium coverages.

(f) The Cl(α) species associated with Ag is found to occupy a preferred site on both potassium- and barium-dosed surfaces, resulting in chemisorptive replacement of O(α) into the subsurface region.

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