Monitoring Super- and Subsurface Oxygen on Ag(210) by High Energy Resolution X-ray Photoelectron Spectroscopy: Subsurface Diffusion and Segregation

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We report on a high energy resolution X-ray photoelectron spectroscopy plus supersonic molecular beam investigation of O/Ag(210). Two components are detected in the O1s spectra upon O2 adsorption, at binding energies $E_b = 527.7$ and 529.6 eV. The former peak persists up to 470 K, while the latter one decreases abruptly above 280 K. Comparison with a previous vibrational spectroscopy investigation on the same system (L. Vattuone, et al. Phys. Rev. Lett. 2003, 90, 228302) allows to assign both features to atomic oxygen. The low-energy peak is identified with adatoms, while the other is correlated to O atoms in subsurface sites. A minor contribution at the same binding energy, due to carbonates, is quantified by inspection of the C1s low-energy peak is identified with adatoms, while the other is correlated to O atoms in subsurface sites. A minor contribution at the same binding energy, due to carbonates, is quantified by inspection of the C1s

Introduction

The fundamental role of defects in determining the reaction rate of many catalytic processes in the heterogeneous phase has been recognized since the very early days of surface science. However a detailed investigation of their action has been addressed only recently, in the attempt of filling the structure gap between surface science experiments (performed in ultrahigh vacuum (UHV) conditions and on nearly defect-free single-crystal surfaces) and real conditions occurring in industrial reactors (high pressure and poorly defined substrates). Artificially defected surfaces can be produced in UHV by damaging a perfect crystal, e.g., by ion bombardment or laser pulses. All kinds of defects are then generated, but the substrate is poorly characterized. Alternatively stepped surfaces, i.e., crystals cut along High Miller Index planes and thus showing a high density of a well-defined, low coordination site, can be investigated. Among the many experimental results on defected surfaces we remember that, using the first approach, a sizable increase of the dissociative adsorption probability was found for NH3 on Ru(0001)2 and for O2 on Ag(100)3. An enhancement of the reactivity was observed also for CO oxidation on Pt(111)4 and ascribed to the increased sticking probability of oxygen. Investigation of Pt(533) revealed the active role of (100) steps in the H2, CH4, and O2 dissociative adsorption dynamics,5 while for O2/Ni(211) a much higher adsorption energy was detected with respect to Ni(111).6

Some of us have recently demonstrated that Ag(410) and Ag(210), vicinal surfaces of Ag(100) characterized by a high density of open steps, show a different chemistry toward O2 adsorption with respect to the flat surface.7,8 The adsorption dynamics of these systems were investigated by the retarded reflector method of King and Wells (KW in the following)9 taking advantage of a supersonic molecular beam, which allows the selection of the translational energy, $E_t$, and the angle of incidence, $\theta$, of the molecules impinging on the surface. The final state of the adsorption products was monitored by means of high-resolution electron energy loss spectroscopy (HREELS). Our main findings were: (a) Dissociation occurs already at a crystal temperature $T = 105$ K while, in absence of steps, adsorption at this temperature is nondissociative.10 Residual oxygen admolecules survive only at terrace sites and are suppressed for the too narrow terraces of Ag(210). (b) Two oxygen adatom species, characterized by vibrational frequencies of 30 and 40 meV, are detected and assigned to O-atoms in 4-fold hollows (O4) and to O−Ag rows at the steps (OStep), respectively. A third vibrational mode at 54−56 meV, disappearing shortly below room temperature, is present only on Ag(210). Density functional theory (DFT) calculations11 identified it with the in-phase vibration of O atoms at the steps and in subsurface octahedral sites (OOcta) against the Ag lattice, a displacement pattern reminiscent of the TO mode of AgO.12 This finding is particularly intriguing since the detailed mechanisms governing the access of oxygen to subsurface sites are still not clear, due to the difficulty in monitoring these species with usual surface science techniques.

For a better understanding of O/Ag(210), we investigated this system by means of X-ray photoelectron spectroscopy (XPS), and we report our findings in the present paper. Previous XPS results on flat Ag(100) showed the presence of two atomic oxygen phases: a $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ surface structure, stable below room temperature, and a $(1 \times 1)$ one, stable above 300 K.13 The former moiety is characterized by a binding energy $E_b = 530.3$ eV and has therefore a covalent nature;14 the latter one, with $E_b = 528.3$ eV, is oxidic. On Ag(110), on the contrary, only one adatom phase with $E_b = 528.1$ eV is detected under UHV conditions.15 For O/Ag(210), we find that two peaks grow in the O1s region upon O2 exposure below room temperature. Their behavior with respect to oxygen dose and crystal temperature confirms the results obtained by vibrational spec-
troscopy\(^8\) and by ab initio calculations,\(^{11}\) allowing to identify these species with supersurface and subsurface oxygen and providing a more complete description of the investigated system.

**Experimental Section**

The photoemission experiments were carried out at the SuperESCA beamline of the ELETTRA Synchrotron radiation source in Trieste.\(^{16}\) The experimental station is equipped with a supersonic molecular beam, which allows the selection of the angle of incidence of the impinging molecules and to vary \(E_i\) by using either pure gases or molecules seeded in an inert carrier. For the experiments reported here, we used a pure O\(_2\) beam (\(E_i = 0.10\) eV) or oxygen seeded in helium (3% concentration, \(E_i = 0.40\) eV). The pure O\(_2\) beam flux, measured by a spinning rotor gauge, read \(\phi = 0.03\) monolayer (ML)/s (1 ML = 1.07 \(\times\) \(10^{15}\) atoms/cm\(^2\)). For the seeded beam, \(\phi\) was calibrated with respect to the pure beam flux, by comparing the O\(_2\) partial pressures in the chamber, and read 0.03 ML/s, too. XPS measurements were recorded while dosing, thus allowing for a time-resolved investigation on a 10-s time scale.\(^{17}\) Oxygen was dosed with the beam impinging perpendicularly to the (210) plane, corresponding to an emission angle \(\theta_{em} = 40^\circ\). To maximize the surface sensitivity and the XPS cross section, the C1s and the O1s regions were investigated with photon energies of \(h\nu = 400\) eV and \(h\nu = 655\) eV, respectively. The overall resolution was 0.15 and 0.30 eV in the two cases. The relative sensitivity to C and O was determined by comparing the signal intensities recorded for CO\(_2\) adsorption. We found that the sensitivity to C is \(7.5\) times larger than for O, in fair agreement with the value estimated from the photoionization cross section and the photon flux at the two primary energies. The energy of the photoemitted electrons is calibrated with respect to the Fermi edge recorded at \(T = 93\) K for each measuring condition. The Ag3d\(_{5/2}\) level reads then 368.25 eV, in agreement with the value reported in the literature.\(^{18}\) Peak areas are calculated via a best-

![Figure 1](image1.png)

**Figure 1.** Schematic drawing of the Ag(210) geometry (top view). The unit cell and the relevant sites for oxygen adsorption are indicated.

![Figure 2](image2.png)

**Figure 2.** XPS spectra recorded while exposing the Ag(210) surface at 110 K to an O\(_2\) beam impinging at normal incidence. Panels A and B refer to a pure beam experiment (\(E_i = 0.10\) eV O1s and C1s regions, respectively), panels C and D to the corresponding experiment performed with a seeded beam (\(E_i = 0.40\) eV). In both cases two peaks grow in the O1s region, the intensity of which depends on beam energy. Inspection of the C1s region reveals little carbonate formation and accumulation of graphitic C, witnessed by the intensities at 287.7 eV and around 284.3 eV, respectively. All the spectra are normalized with respect to the acquisition time and scaled to the photon flux of the seeded beam experiment. To improve the quality of the data each spectrum of the O1s region is the average of three subsequent scans recorded during time-resolved experiments and showing no significant differences in the peak intensities.
fit procedure assuming a Doniac–Sunjic function convoluted with a Gaussian to model the shape of the peaks. The estimated error in the determination of the peak position is 50 meV. The relative error on the calculated areas is between 5 and 20%, depending on the quality of the original spectra and being higher for time-resolved experiments, in which the signal-to-noise ratio is slightly degraded by the reduced integration time. For the weakest signals at 529.6 eV the relative error reaches 50%.

The Ag sample is a 7 mm diameter disk cut within 0.1° off the (210) plane. Its structure is schematically reported in Figure 1: it consists of alternated, 1-atom-row-wide (100) and (110) nanofacets and is therefore characterized by a 50% density of open steps. By definition of $\theta = 0°$ as the normal to the (210) surface, $\theta = -26.5$ and 18.5° correspond to the local normal to the (100) and (110) nanofacets, respectively. Before each experiment the sample was prepared by sputtering cycles followed by annealing to 700 K until no contamination is detected by XPS and a sharp low-energy electron diffraction (LEED) pattern is observed. Residual traces of carbon are removed by O$_2$ exposure at 600 K.

Figure 2 shows the evolution of the O1s and C1s regions during O$_2$ exposure of the Ag(210) crystal at $T = 110$ K. O$_2$ is dosed by the supersonic molecular beam at normal incidence with energies $E_i = 0.10$ eV (panels A and B) and 0.40 eV (panels C and D), respectively. Two peaks grow with O$_2$ exposure ($\chi_{O_2}$) in the O1s region around 527.7 and 529.6 eV. After comparable doses, the overall intensity is higher for the higher-energy beam, in accord with previous data showing that adsorption is globally activated. Previous HREELS results allow the assignment of both features to atomic oxygen. Inspection of the C1s region at the end of the dose (panels B and D) reveals that a small amount of carbonates ($E_b = 287.7$ eV) has accumulated during the oxygen uptakes. The corresponding O1s line is expected at 529.9 eV, thus giving a marginal contribution to the 529.6 eV peak intensity. Little graphitic carbon has formed around 284.3 eV, in particular for the pure beam experiment. Contamination with C-containing

**Data Presentation**

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species may arise either from CO coadsorption from the rest vacuum or from C segregation from the bulk.

Parts A and B of Figure 3 report the areas of the oxygen related peaks vs $\lambda_{O_2}$ for the uptakes reported in Figure 2 and for the short exposure shown in Figure 5C. For the 527.7-eV species (panel A), the adsorption probability, corresponding to the slope of the curves, is initially high and decreases after a few ML exposure. The initial sticking coefficient increases by a factor $10$ between $E_i=0.10$ and $0.40$ eV, in accord with the estimate for the total sticking probability evaluated by KW investigation.$^{19}$ The slope of the 529.6-eV curve (panel B), on the contrary, is nonzero up to large exposures. The total oxygen coverage, $\theta$, can be estimated from the area of the XPS peaks once it has been calibrated with respect to the $\theta$($\lambda_{O_2}$) curve measured in identical conditions by KW. By assumption that both oxygen moieties have the same photoemission cross section, we estimate after $\lambda_{O_2}=30$ ML at $E_i=0.40$ eV (0.10 eV) an atomic oxygen coverage of $0.25$ ML (0.14 ML) for the 527.7-eV species and of $0.09$ ML (0.04 ML) for the 529.6-eV species. In Figure 3C, we plot the 529.6-eV peak area as a function of the 527.7-eV peak area, thus showing the correlation between the two oxygen-related features. The curves for the pure and the seeded beam merge around a 527.7-eV area of $0.3$, showing a plateau between $0.3$ and $0.5$. The $E_i=0.10$ eV experiment is therefore likely to be equivalent to very low exposures performed at $E_i=0.40$ eV. No superstructures were observed by LEED.

Figure 4 shows the position of the O1s peaks vs peak area (proportional to the partial coverage of the oxygen moieties) for the experiments of Figure 2. Panel A refers to the low-energy feature, panel B to the one around 529.6 eV. The energy of the former peak is slightly lower when dosing O$_2$ with $E_i=0.10$ eV and shifts up with partial O coverage, moving from 527.4 to 527.6 eV for the pure beam and from 527.6 to 527.9 eV for the seeded beam. Such behavior suggests the presence of at least two O species contributing to the 527.7-eV intensity, which are populated differently depending on dosing conditions. The trend for the 529.6-eV peak is less clear due to the larger scatter of the data, but the $E_i(\theta)$ curve is essentially flat.

Figure 5 shows the thermal evolution in the O1s and C1s regions of O/Ag(210) layers produced at $T=110$ K and annealed to different temperatures. The reported experiments refer to: (AB) 30.3 ML exposure with $E_i=0.10$ eV (from the spectra of parts A and B of Figure 2); (CD) 0.3 ML exposure
with $E_i = 0.40$ eV; (EF) 29.2 ML exposure with $E_i = 0.40$ eV (see parts C and D of Figure 2). We notice that:

(a) The 529.6-eV peak grows strongly with temperature and decreases abruptly between 250 and 300 K. The effect is better observed in the experiment of panel C due to the negligible carbonate contribution to the 529.6-eV peak. In these conditions, a definite shift of the 527.6-eV peak to 527.8 eV occurs below 200 K.

(b) Only a small fraction of the increased 529.6 eV signal comes from depopulation of the 527.8 eV moiety, since the latter intensity is little affected by crystal temperature. Most of the 529.6-eV oxygen must therefore come from segregation from deeper layers.

(c) The carbonate signal grows with $T$ in all experiments, remaining stable up to $T = 370–400$ K, depending on coverage.

(d) A peak at $E_b = 282.7$, assigned to carbidic carbon, forms for the pure beam experiment. Its intensity grows up to 280 K and disappears around room temperature. Most probably also these traces of carbidic carbon originate from segregation from the bulk, but we have no explanation why this phenomenon is induced only when oxygen is deposited by the low-energy beam. Because this point is marginal for the present investigation, it was not investigated further.

**Discussion**

HREELS results for the same system showed that three different atomic oxygen moieties are present, giving rise to losses at 30, 40, and 54–56 meV. The 30-meV species, stable only below 200 K, is assigned to oxygen adatoms in 4-fold hollow sites ($O_h$) of the (100) nanoterraces. The 40-meV loss was attributed to O atoms decorating the steps ($O_{step}$) as confirmed by DFT calculations. Population of $O_{step}$ dominates at low $E_i$ since occupation of the 30-meV site is more strongly activated. The 54–56-meV loss grows in intensity and shifts to 58 meV when annealing the crystal, and it disappears abruptly slightly below room temperature. DFT calculations demonstrated that it is associated to the in-phase vibration of oxygens at the step edge and in octahedral subsurface sites ($O_{octa}$) against the Ag lattice. Moreover XPS inspection of the C1s region indicates a small carbonate contamination. A fourth oxygen species ($O_{carb}$) must therefore be present on the Ag(210) surface and contribute to the 529.6-eV intensity.

Only two features appear, however, in the O1s region upon O$_2$ exposure. Their intensity is reported vs $T$ in Figure 6 (upper panels). The low-energy peak is found between 527.4 and 527.9 eV, depending on dosing conditions, partial O coverage, and annealing temperature, and it is stable up to $T = 470$ K. The behavior of the 529.6-eV peak, on the contrary, follows closely the one of the 56-meV vibration ($O_{step} + O_{octa}$). For a fair comparison with the corresponding HREELS, we need however to deconvolute the XPS peak, isolating the contribution of carbonates. This was done by calculating the $O_{carb}$ intensity from the corresponding C$_{carb}$ signal at 287.7 eV; the result is reported in the lower panels of Figure 6. We notice that:

(a) since the sensitivity to C is approximately 7.5 times larger than the one for O, carbonates are always a minor contribution to the 529.6-eV intensity. From comparison with the O1s intensities and taking into account the difference in photoionization cross section and photon flux for O and C, we estimate a maximum CO$_3$ coverage <4 $10^{-3}$ ML, which would have escaped detection with most surface analysis techniques. In fact no carbonate related losses were detected by HREELS in ref 8. Most of the intensity at 529.6 eV is thus due to an atomic oxygen species, which disappears shortly below room temperature;

**Figure 6.** Upper panels: Area of the 527.7-eV (circles) and 529.6-eV peaks (squares) vs $T$ calculated for the three experiments shown in Figure 5. Bottom panels: $O_{carb}$ and $O_{octa}$ contributions to the 529.6-eV peak, calculated as explained in the text. The carbonate signal persists up to 370–400 K (continuous arrow in panel F), while subsurface oxygen disappears above 280 K (dashed arrow). Two sets of data are reported for the low $E_i$ experiment.
carbonates justify the persistence of some signal at 529.6 eV above $T = 300$ K.

(b) The delayed growth of the 529.6-eV peak with respect to the 527.7-eV moiety (see Figure 3C) is compatible with the behaviour of the 56-meV peak in the corresponding HREELS experiments.\(^8\) According to theory, it is due to the $O_{\text{step}}$ precoverage needed to open up the channel leading to subsurface sites. Two onsets are present at 527.7-eV peak areas of $\sim$0.3 and 0.5, corresponding to $\Theta \approx 0.12$ and 0.25 ML, respectively, and a strong increase of the 529.6-eV area takes place when the 527.7-eV moiety is close to saturation coverage. Points a and b allow therefore to identify the atomic oxygen species with $E_b = 529.6$ eV with atomic oxygen in subsurface octahedral sites, which are efficiently populated only after a critical coverage is reached.\(^22,23\)

(c) The dependence of the low-energy peak position on experimental conditions suggests that this signal arises from the superposition of at least two photoemission lines. Moreover, it disappears above 500 K, in accord with the onset of $O_{\text{octa}}$ species have very similar O1s binding energies, contributing to the antiphase behavior observed by HREELS for the occupation of $O_2$ and $O_{\text{step}}$. Discriminating between the two moieties is however not easy since their binding energies are very close. The upshift with temperature and/or coverage may indeed be due to a change in their relative population.

(d) The small, but reproducible, reduction of the peak at 527.7 eV associated to the growth of intensity at 529.6 eV suggests that most of the $O_2$ moves subsurface at 200 K, in accord with the antiphase behavior observed by HREELS for the occupation of $O_2$ and $O_{\text{octa}}$ sites at different angles of incidence.\(^3\) The weak increase of the same peak when annealing above 280 K is indicative, on the other hand, that some $O_{\text{octa}}$ moves back to supersurface sites, although most of it dissolves into the bulk.

(e) The changes in the intensity of the subsurface oxygen signal with crystal temperature are definitively much larger than those of the 527.7-eV peak. This effect is particularly evident in Figure 6C and suggests that O dissolved into the bulk segregates and is stabilized in the subsurface region by the presence of oxygen adatoms. Such hypothesis is supported by several theoretical studies both on $Ag(100)$\(^22,24\) and on Cu.\(^25\) In accord with this interpretation, no oxygen segregation was observed when heating a clean crystal. Adsorbate-stabilized segregation was invoked also for the formation of an oxide phase when treating O/Ag(100) above 160 K with CO.\(^26,27\) but no signature of surface oxide formation is detected in the valence band region in the present case.

Conclusions

The O/Ag(210) system is investigated by means of XPS and supersonic molecular beam. The observed peaks correlate well with the atomic oxygen species identified by HREELS measure-ments\(^8\) and by ab initio calculations.\(^11\) We find that supersurface species have very similar O1s binding energies, contributing to an unresolved peak around 527.7 eV. $O_{\text{octa}}$ on the contrary, is characterized by $E_b = 529.6$ eV. Little carbonates form upon oxygen exposure and upon annealing the oxygen adlayer. Oxygen segregation from the bulk to the subsurface region is observed when mobility is activated and when the subsurface site is stabilized by oxygen adatoms. The combination of our previous HREELS results and of the present XPS investigation gives a complete characterization of the O/Ag(210) system.

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