Subtle interaction between Ag and O₂: a near ambient pressure UV photoelectron spectroscopy (NAP-UPS) investigations

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MS received 28 October 2017; revised 26 December 2017; accepted 15 February 2018; published online 2 March 2018

Abstract. The Ag-O₂ interaction, which is at the center-stage of Ag-catalyzed partial oxidation reactions, is studied with NAP-UPS up to 0.2 mbar O₂ pressure between 295 and 550 K. Three temperature regimes were identified for distinct Ag-O₂ interaction, which are (a) 295–390 K, where mainly dissociative chemisorption of O₂ happens, (b) 390–450 K, where diffusion of O-atoms into the sub-surfaces of Ag is prominent, and (c) >450 K, where metastable oxide forms on polycrystalline Ag surfaces. The work function (WF) of Ag changed from 4.95 (≤390 K) to 5.30 eV (390–450 K), and then to 5.7 eV (≥450 K) at 0.1 mbar O₂ pressure. Oxygen population in the sub-surfaces imparts crucial modifications to Ag at 390–450 K; it makes the surface to be electron-deficient that relates to the change in the WF of Ag and facilitates the formation of space charge layer on Ag surface. Oxygen adsorbed on such modified Ag-surfaces is electrophilic in nature, and this appears at a higher binding energy in core level XPS than the chemisorbed oxygen on metallic Ag. This is supported by angle-dependent NAP-XPS studies. The subsurface population of oxygen in Ag no longer persists at >410 K when the O₂ supply is removed. A high ratio of antibonding/bonding O 2p bands suggests the unique silver-oxygen interaction under the measurement conditions.

Keywords. Epoxidation; heterogeneous catalysis; surface science; electronic structure.

1. Introduction

Silver is an important catalyst for two technologically important partial oxidation reactions, namely, ethylene to ethylene oxide (EtO) and methanol to formaldehyde production.^{1–3} Ethylene to EtO conversion mostly takes place on supported silver catalysts. The reaction is a kinetically controlled selective oxidation.^{1,4} Despite being more prone to combustion than ethylene, EtO formation is high, but in a narrow temperature regime (430–500 K). Oxygen interaction with silver has a crucial role in controlling the EtO selectivity. For the last fifty years, theoretical^{5–8} and experimental^{9–11} investigations led to various models of Ag-O₂ interaction to explain its role in the partial oxidation reactions catalysed by silver; however, the mechanism still remains debated, particularly regarding the nature of oxygen

involved in the activation of ethylene and the nature of silver surfaces under reaction conditions.^{6,12–16}

The process of EtO (or any epoxide) formation, which involves the insertion of oxygen into the π -bond of ethylene (alkene) molecule, requires a ‘special’ oxygen which can activate the alkene. Campbell *et al.*,^{17,18} studied ethylene epoxidation by varying four reaction parameters like the temperature, the partial pressure of oxygen and ethylene, and surface oxygen coverage (θ_o), and a reaction model was proposed. It suggests that under isothermal conditions, θ_o plays the major role in the epoxide selectivity. Theoretical calculations by van Santen *et al.*,^{1,15} shows that dissolved O-atoms in the subsurfaces of Ag is responsible for epoxidation over complete combustion by Ag catalysts. The presence of dissolved oxygen species in the subsurfaces of Ag facilitates, (a) the reduction in bond energy of adsorbed oxygen on silver, and (b) modifies the repulsion of adsorbed oxygen atoms and adsorbed ethylene into an attractive one.

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According to thermodynamic studies, the active oxygen species in ethylene epoxidation over Ag catalysts is a weakly bound species under steady-state conditions,^{1,6} and *in situ* techniques are indispensable for its detection. A series of articles^{4,5,10,12} on *in situ* characterization are available that reports the nature of active species, oxygen adsorption site, and reaction intermediates. X-ray photoelectron spectroscopy (XPS) studies under *in situ* conditions are available in the identification of the active oxygen species. Bukhtiyarov *et al.*, reported that electrophilic and nucleophilic oxygen species are present on the catalytically active surface under epoxidation conditions.¹² In the O 1s spectra, the components at 528.5 and 530.2 eV binding energy (BE) were attributed to the nucleophilic and electrophilic oxygen, respectively. The nucleophilic oxygen leads to the total combustion of ethylene, whereas the electrophilic oxygen is active for partial oxidation. The nature of nucleophilic oxygen was studied earlier,¹⁹ whereas the role of electrophilic oxygen is inconclusive. The fact is that even the *in situ* near ambient pressure XPS measurements carried out so far were not able to detect any charge transfer between Ag and O;^{5,12} In fact, Ag 3d core level shows no change in the present and earlier studies. However, probing the valence band (VB) with low energy photons (He-I source; $h\nu = 21.2$ eV) reveals many crucial changes in Ag-O₂ interaction, which otherwise remain untraced in core level XPS.

VB photoelectron spectroscopy with low energy photons is an important tool to access mostly surface specific electronic changes. Indeed, near ambient pressure (NAP) ultraviolet photoelectron spectroscopy (NAP-UPS) is fully relevant to explore silver-oxygen interaction, since Ag 4d and O 2p orbitals exhibit high photoionization cross sections (σ) of 16.62 and 10.67 Mb, respectively, with He-I (21.2 eV) photon.²⁰ The changes observed with He I excitation is not possible to detect with Mg or Al K α , due to, (a) three to five order of magnitude smaller σ for Ag 4d (0.1030 with 800 eV; 0.021 Mb with Al K α photons), and O 2p (0.0022 with 800 eV; 0.00024 Mb with Al K α photons); (b) low resolution of X-ray; and (c) comparatively high probing depth of X-ray photons. Earlier VB studies on Ag were carried out in vacuum^{21,22} or at low pressure ($\leq 10^{-4}$ mbar),²³ whereas NAP-UPS is able to measure under more practical *in situ* conditions. *In situ* NAP-UPS analysis provides the information about the work function (WF), Fermi energy (E_F), chemical bonding, etc. This information is very important to determine the nature of oxygen present on the Ag surfaces under high-pressure conditions.

In the present work, the NAP-XPS and NAP-UPS data was employed to understand the silver-oxygen

interaction and subsequent electronic structure changes in the critical epoxide formation temperature conditions. Three temperature regimes have been identified, and the silver-oxygen interaction changes drastically from one to another regime. Present NAP-UPS analysis provides the direct evidence of subtle Ag – O₂ interaction in the active temperature window of 390–450 K for epoxidation. As the temperature reaches 390 K, the oxygen begins to diffuse into the subsurface layers of Ag, which makes the silver surface marginally cationic and it is confirmed from the work function change as well as angle-dependent NAP-XPS. It has also been observed that between 390 to 450 K, the oxygen coverage on Ag surface decreased significantly, in spite of the presence of large excess of gas-phase oxygen (0.1 mbar). On the basis of these observations, it is suggested that the modified surface attract the electron-rich alkene molecules and facilitates alkene adsorption and subsequent epoxidation. The present study contributes significantly to understand the gas-solid interaction at several orders of pressure higher than the conventional surface science measurements²⁴ at high vacuum (10^{-9} mbar) and hence closer to the actual conditions (10–30 bar).^{25–32}

2. Experimental

The experiments were performed with a custom-built lab-based near ambient pressure photoelectron spectrometer.^{27,31} The setup is equipped with a differentially pumped electron energy analyzer R3000HP (VG Scienta). In contrast to the many such systems employed with the closed high-pressure cell, the system employed for the present studies involves an open reactor design. High-pressure gas doser extends right up to the Ag-surface and *in situ* pressure measurements made very close to the surface ensures that the pressure values reported are highly reliable. More information about the NAP- photoelectron spectrometer is described in refs.^{27,31} An x-ray monochromator (with Al K α), a Mg-Al twin anode source, and a differentially pumped helium discharge lamp (for He I and He II excitations) are available as photon sources. In this setup, the samples can be analyzed up to a total pressure of 1 mbar with x-ray sources and up to 0.4 mbar with UV source²⁷ from 100 K (with liquid nitrogen) to 1023 K with suitable sample holders. A polycrystalline foil of Ag (purity 99.999%, MaTeck, Germany) was used for the present studies. The samples were cleaned by argon ion sputtering by applying a potential of 3 kV and an acceleration current of 6 mA to the sputter gun, followed by annealing at 1000 K. A series of sputter-anneal cycles produced clean silver surfaces. No contamination of oxygen and carbon was detected by XPS/UVPEs. The impurity level of any sulfur, silicon, and phosphorous was lower than the detection limits of R3000 analyzer. Detailed O₂

- Ag gas-solid interaction experiments were carried at 0.1 mbar oxygen (99.99%) partial pressure from RT (295 K) to 500 K. Similar but representative studies were carried out at 0.2 mbar O_2 pressure also. A cone with 1.2 mm aperture was fitted to the entrance column of the R3000HP analyzer, and a sample to aperture distance of 1.5 mm was maintained for the present measurements. The spectra were deconvoluted with Gaussian-Lorentzian type synthetic components after subtracting a Shirley type background in CasaXPS. All the spectra were calibrated with respect to the Fermi level (E_F) of Ag. The spectra obtained at elevated pressures and temperatures were intensity-normalized with respect to the spectrum obtained under vacuum and at RT.

3. Results and Discussion

3.1 Comparison of VB spectra in UHV and at 0.1 mbar O_2

Figure 1 shows the VB spectra of (a) a clean Ag surface recorded at RT (295 K) in UHV and (b) in the presence of 0.1 mbar O_2 . Gas-phase molecular oxygen recorded at RT is given for comparison in Figure 1c. Ag 4d band observed for a clean silver has three distinct features between 3.8 and 7 eV and metallic E_F feature at 0 eV; the spectrum is in good correspondence with that of reported in the literature.^{22,33–35} The hump observed between 6.8 and 7.6 eV relates to the mixing of the density of states of Ag 4d and 5s orbitals; this is fully supported by the experimental XPS VB studies with high energy photons ($h\nu = 7912$ eV) in combination with DFT studies.³⁵ In fact, it is known that the outermost s orbitals (of coinage metals) penetrates so deep and hence it is worth exploring further;^{36,37} however, early transition metals do not show this trend. A broad and low-intensity peak at ~ 2.6 eV is a satellite peak due to the secondary He I_B radiation (excitation energy 23.06 eV).³⁸

The exposure to oxygen at 0.1 mbar pressure at 295 K (Figure 1b) broadens the Ag 4d features to such an extent that only a single broad feature was observed without any fine structure (as on clean surface). In addition, a new and broad peak appeared between ~ 2.3 and 4.0 eV; indeed this feature was not present on the clean Ag surfaces. Dissociative adsorption of molecular oxygen occurs on the Ag surface at room temperature and forms the metal oxide pair. Oxygen covered islands are indicated to be present (discussed later) and lead to metal oxide pair. The new peak observed between 2.3 and 4 eV is due to the contribution from hybridization between O 2p antibonding and Ag 4d orbitals and assigned to π -antibonding orbital. Another low intensity and broad peak was observed at 8.8 eV, which

Figure 1. Valence band spectra of silver surface recorded. (a) in UHV, and (b) at 0.1 mbar O_2 partial pressure at RT. (c) Gas-phase molecular oxygen spectrum is given for comparison.

is attributed to hybridized bonding feature between O 2p bonding and Ag 5s orbitals.^{15,21} Indeed Ag 4d is a fully-filled *d* band and no formal hybridization with Ag 4d is expected. Both observations are attributed to the formation of metal oxide pair and associated charge transfer from silver metal to oxygen to form oxide anion. O 1s spectrum supports the formation of oxide (O^{2-} appearing around 530 eV) and without any superoxide/peroxo species (Figure 6). The difference spectrum calculated between Figure 1b and 1a after normalization is (shown in Figure S1 in Supporting Information) expected to show the contribution due to metal oxide pair formation and information about, particularly, sigma orbitals of the metal-oxide pair. One of the star marked features could be the energy position of sigma orbital. Large electron donation from Ag surface to oxygen and a significant redistribution of electrons is evident from the difference spectrum.

Gas phase features of oxygen on Ag surface appears between 7 and 8 eV, which is different from pure gas phase oxygen peaks that appear between 7.5 and 8.5 eV (Figure 1c). The vibrational features of the pure gas phase oxygen and oxygen in the presence of Ag, shows the same width which indicates a homogeneous nature of the surface silver atoms on the sample. A shift by

0.3 eV to low BE is due to the surface potential of Ag (Figure 1b). No change in intensity of the E_F characterizes a largely metallic Ag surface (Figure 1b).

3.2 Temperature dependent Ag-O₂ interaction

Figure 2a provides a set of temperature dependent VB spectra recorded on Ag surface from 295 to 500 K at 0.1 mbar O₂ pressure. From 295 to 350 K, no change was observed. At 370 K, the gas phase features of oxygen begin to broaden and shift to 7.4 eV. BE of the most intense O₂ vibration feature is always referred to indicate the changes observed unless indicated. Ag 4d features were unchanged whereas the intensity of O 2p, at 3.35 eV, decreased. These observations indicate an onset of change in the electronic nature of silver surfaces under the measurement conditions. The E_F intensity did not change.

When the temperature was raised to 390 K, (a) gas phase O₂ vibrational features were observed to be less intense, broadened, and shifted to 7.24 eV (Figure 2a), and (b) Intensities of bonding and antibonding O 2p features decreased, while features of Ag 4d remain

unchanged. Substantial changes were recorded when the temperature was raised to 410 K. (1) WF of the Ag surface increased sharply from 4.95 eV (up to 390 K) to 5.30 eV (Figure 4). (2) The intensity of the O 2p antibonding and bonding features sharply decreased (Figure 2b) which indicated that the surface θ_0 is low, even in the presence of large excess of O₂. (3) Ag 4d band peaks at a higher intensity, particularly for the first two components (Figure S2 for the deconvolution of the spectra obtained at 295 and 410 K). (4) The gas phase O₂ vibrational features further broadened and shifted towards lower BE to 6.9 eV, indicating the change in nature of the surface to be heterogeneous in character. The change in WF of Ag by 0.35 eV and the change in BE of vibrational features of oxygen on Ag (0.34 eV) are found to be in good correlation. The change in WF indicates a discreet change in the electronic nature of the Ag surface. (5) E_F intensity remains unchanged. All these observations are fully reversible to metallic Ag, when the O₂ supply was cut-off (*vide infra* Figure 5). It underscores the dynamic changes that occur on the Ag surface in the presence of oxygen. Even if Ag is exposed to plenty of O₂, the intensities of Ag 4d increases and

Figure 2. (a) Valence band spectra of Ag recorded with He I excitation as a function of temperature at 0.1 mbar O₂. Note a decrease in the intensity of antibonding and bonding O 2p features at 3.15 and 9.5 eV at 410 K with shifts in BE are indicated by dashed and solid arrows, respectively. Similar results observed at 0.2 mbar is shown in Figure S3 (in Supplementary Information). (b) The contribution from O 2p antibonding band at 0.1 mbar oxygen is plotted against the temperature. (c) Ag 4d/O 2p intensity ratio is plotted as a function of temperature.

O 2p antibonding decreases; this reflects the unique change that occurred on the surface. Except gold, any other transition metals get oxidized irreversibly under the present measurement conditions; however, the above reversible nature highlights the unique nature of Ag-O₂ interaction. We attribute this change with the diffusion of chemisorbed O-atoms into the immediate sub-surfaces of Ag, which modifies the WF of Ag. A dynamic equilibrium among the oxygen adsorption, O atoms diffusion into the sub-surfaces of Ag, and oxygen desorption is considered at and above 400 K. No detection of silver oxide (Ag₂O) was observed in the present experimental conditions; this also supports the above conclusion (Figure 5).

With further increase in temperature to 430 K at 0.1 mbar O₂, the intensity of oxygen antibonding and bonding features increased; however, antibonding feature shifted to lower BE (3.1 eV) and bonding feature shifted to higher BE at 9.5 eV. This is due to the reactive nature of antibonding O 2p band at 3.15 eV, and less reactive and stable nature of bonding O 2p band at 9.5 eV. Ag 4d features are similar to that of recorded at 410 K. The O₂ gas phase feature shifted further down to 6.8 eV, and there is no significant change in the WF of Ag. The possibility of any interference due to impurities, like carbon or formation of carbonate²⁸ species, which are likely concerns with a typical high-pressure cell, is absent in the present measurements. No C-species observed in the C 1s spectrum (data not shown) reiterates the clean Ag-surface. Within the range of 450 to 500 K at 0.1 mbar, the following changes were recorded. (a) The WF of Ag increased from 5.30 (410–440 K) to 5.70 eV (450–500 K). (b) The intensity of the bonding and the antibonding O 2p features further increased, and it is comparable to the intensity observed at 350 K. O 2p antibonding feature is narrow at 450–500 K, compared to that of at ≤ 430 K. NAP-UPS spectra recorded at 0.2 mbar O₂ pressure (Figure S3a) shows the similar trend. Except a significant decrease in E_F intensity at 500 K, no other important change was observed at 0.2 mbar (Figure S3b). (c) Increase in the WF of Ag and temperature affects further downshift of the oxygen vibrational peaks, and they merged with Ag 4d features. Increase in WF at 450 K as well as the appearance of O 2p bands at different BE demonstrates the change in the nature of the surface due to electronic as well as chemical reasons. A similar observation of the change in WF of Cu due to the formation of Cu_xO with oxygen was reported earlier.²⁷ In fact, a mere 0.6 eV shift was observed on the Cu₂O formation with O₂ vibration features, whereas 0.9 eV shift was observed at 450 K just with O-diffusion into Ag sub-surfaces. It is very likely that the Ag surface undergoes a dynamic partial oxidation. A

further increase in temperature up to 650 K does not show any change in the VB (results not shown).

In each set of temperature dependent measurements, three important characteristics were common: (a) Above 400 K, when the oxygen supply was cut-off, all the oxygen-induced changes to disappear, and the surface returns to its original metallic state. It indicates that the presence of oxygen is essential to observe a reversible and dynamic change on the Ag surface. A fast decrease in oxygen-related features observed on increasing the temperature above 500 K after oxygen dosing at 0.1 mbar at 410 K is shown in Figure S4 (in Supplementary Information). More drastic changes are expected at high pressures under industrial epoxidation conditions. (b) Albeit the intensity changes, Ag 4d band always appear between 4 and 7 eV and shows hardly any shift, irrespective of the applied temperature and oxygen pressure (between UHV to 0.2 mbar O₂ pressure and up to 600 K). These two observations indicate a subtle and unique interaction of oxygen with Ag under the present reaction conditions. The constant E_F intensity of Ag under the measurement conditions also supports this (Figure S4). Gold, within group IB elements, possesses similar characteristics and shows hardly any interaction with O₂. However, under such comparable measurement conditions, Cu is prone to form its oxides (Cu₂O and CuO).^{27,31}

Figure 2b shows a relative quantification of O 2p antibonding intensities at different temperatures. The integrated peak area at 295 K was considered as 100% oxygen coverage (θ_0) on Ag-surface. With reference to this, other areas were given in relative percentage and are plotted as a function of temperature. The first drop in relative θ_0 at 350 K does not accompany any change in WF. Nonetheless, the second and major change between 390 and 410 K accompanies with a change in θ_0 and WF of Ag. At 450 K, the θ_0 again increases to the values similar to that observed at 350 K, but with a change in silver WF.

The intensity ratio of Ag 4d to antibonding O 2p features was estimated (Figure 2c) to complement the result shown in Figure 2b. First two deconvoluted peaks of Ag 4d (Figure S2) were considered for this plot. The calculation with the total Ag 4d intensity does not change the trend, shown in Figure 2c. Three temperature regimes identified earlier is observed in Figure 2c also, reiterating the earlier conclusions. Even though a large amount of gas phase oxygen is available, an unusual decrease in the O 2p feature between 390 and 450 K is partly attributed to diffusion of O atoms into the immediate sub-surfaces of Ag. Although oxygen desorption could occur at and above 400 K, this does not

support the change in WF observed in this temperature window. Further, no impurity such as carbon, carbonate species were observed under the above conditions. ≥ 450 K metastable surface oxide forms and the strong O 2p bonding and antibonding features support this conclusion. This is also evidenced by the decrease in Ag 4d/O 2p ratio (Figure 2c). A valley observed between O 2p and Ag 4d features in UVPES deepens further at and above 450 K due to increase in the energy difference between them (Figure 2a), and WF changes from 5.3 (410 K) to 5.7 eV (≥ 450 K). On the basis of these results, it can be concluded that the silver surface has become significantly cationic with the formation of metastable oxide on the surface. Although metastable oxide formation is suggested ≥ 450 K, it is highly dynamic in nature; the surface shows well resolved Ag 4d features when oxygen was evacuated.

Figure 3a is an enlarged view of oxygen vibration features recorded at different temperatures. The vibrational features are characteristic of the Schumann-Runge bands observed in the ultraviolet region around 175–205 nm.³⁹ As explained above, these narrow vibration features shift towards lower BE, due to the influence of silver surface potential on the molecules vibrating close to it. It is to be noted that vibration features are from free O₂ molecules in the gas-phase, but close enough to the surface to sense the electronic changes occurring on the Ag-surface. The broad features observed at $T \geq 390$ K is partly due to surface inhomogeneity,

in view of O-diffusion into the sub-surfaces. This is further supported by the gas phase spectrum of *in situ* heated oxygen shows no significant broadening between 300 and 500 K (Figure S5 in SI).²⁵ Surface potential influencing Ar 2p core level was recently reported by Axnanda *et al.*⁴⁰ It is also very interesting to underscore that, in contrast to the expectations of surface potential influencing very limited layers of gas-molecules (of the order of nanometers), surface potential exerts its influence much farther (several hundred microns). This aspect is worth investigating further in a systematic manner.

BE of the most intense Schumann-Runge band is plotted as a function of temperature in Figure 3b. A shift toward lower BE was observed above 350 K, compared to RT value. Sharp changes observed at 410 and 450 K are due to the change in the surface potential of Ag, accompanied by a change in WF of the Ag surface. The full width at half maximum (FWHM) of oxygen vibrational features is plotted in the inset of Figure 3b. Increase in FWHM supports the chemical and electronic changes that occur on the surface due to interaction with oxygen. A careful look at the vibration profiles shows that the peak splits into two features at and above 390 K. The heterogeneous nature of the Ag surface imparts such changes. Based on the above observations, we propose that the sub-surface oxygen population cannot occur in a continuous film; however, it grows into macroscopic size islands with increasing temperature. Due to the

Figure 3. (a) Gas phase vibrational features of 0.1 mbar oxygen on Ag is plotted against the temperature. (b) Change in the binding energy of the most intense vibrational peak of O₂ is plotted as a function of temperature. The change in FWHM of O₂ vibration feature with temperature is shown in the inset.

heterogeneous distribution of subsurface oxygen, two different surface Ag sites form, one with the presence of subsurface oxygen in its coordination, and the other without any subsurface oxygen. Nonetheless, overall (or average) surface potential also seems to change, which is reflected in the BE shift of oxygen vibrational features. This indicates that epoxidation, as well as combustion of alkenes, are possible simultaneously on such heterogeneous surfaces. However, this needs to be explored by *in situ* microscopy under relevant conditions.

3.3 Temperature dependent work function changes

Figure 4 shows the secondary cut-off of the Ag VB spectra. The changes in Ag WF at different temperatures are evidently noticeable. The onset of a change in WF begins around 390 K and it increased sharply at 410 K. The second major change in WF was observed at 450 K which remains stable up to 650 K. No change in O₂ vibrational features and WF of silver observed below 370 K indicate that the nature of the Ag surface is largely unaffected in this regime and it remains largely metallic in nature. Low oxygen desorption temperature at 400 K marks this type of oxygen, which is neither active for epoxidation or combustion.²¹ The results discussed above categorize three separate temperature regimes, where each temperature regime has a distinct nature of the interaction between O and Ag. It is also to be mentioned that

the WF measurements were made at an applied bias of 3 V (data not shown). Same WF values were obtained with (after correcting values for) applied bias or without bias further supports the actual change in WF due to gas-solid O₂-Ag interaction and consequent electronic changes.

3.4 Subtle silver-oxygen interaction

A simple experiment was carried out to understand the nature of antibonding O 2p π -band. Silver surface was exposed to 0.1 mbar O₂ at 350 K and the NAP-UPS was measured. Subsequently, oxygen was evacuated and UPS was measured simultaneously at different temperatures, and the results are shown in Figure 5. On gradually increasing the temperature, the intensity of O 2p features decrease while the features of metallic silver reappears ≥ 350 K. A simple comparison of spectra recorded in UHV and at 0.1 mbar O₂ pressure (Figure 2a) fully supports this observation. Critically, no change in WF was observed at 400–420 K, and this underscores that the metallic nature of the silver surface is fully restored. It is also to be reiterated that WF changes occur exclusively in the presence of oxygen, and no changes observed under UHV conditions further supports the subtle interaction between silver and oxygen. Another point to be highlighted is the large intensity ratio of antibonding to bonding O 2p character

Figure 4. Work function measured as a function of temperature at 0.1 mbar oxygen and for clean Ag in UHV at 295 K. The work function of Ag changes from initial 4.95 to 5.3 eV at 410 K and to 5.7 eV at 450 K.

Figure 5. UVPES recorded at 0.1 mbar O₂ at 350 K followed by evacuation to UHV and spectral recording at different temperatures. The weakly bound oxygen desorbs and the metallic features of silver revert back gradually.

(between 5 and 11) across all temperature regions. This also directly indicates that the oxygen present on the surface is ready to desorb when the oxygen supply was cut-off and makes the Ag-O₂ interaction as the unique one.

The diffusion of O atoms into the immediate sub-surfaces makes Ag marginally cationic (Ag^{δ+}) in nature; it is to be noted that the diffused oxygen is present as O²⁻ (Figure 6) as counter anion to the Ag^{δ+}. This cationic nature creates a space charge layer on the Ag surface and possibly induces a semiconductor-like character.⁴¹ As predicted by van Santen *et al.*,¹⁵ Ag^{δ+} character is expected to change the repulsive behaviour of alkenes toward Ag to an attractive one ≥ 390 K. In fact, a decrease in the O 2p antibonding character and a shift towards lower BE (Figure 2) hints an imminent enhancement in reactivity. A comparison between Figures 2b and 2c shows an apparent inverse correlation among them. Angle-dependent XPS studies on oxygen interaction with Ag(111) surface too indicates the O-diffusion into subsurface at 420 K.⁴²

3.5 Core level studies

Figure 6 shows O 1s core level spectra recorded at 0.2 mbar O₂ pressure between 295 and 500 K. Very similar to VB, O 1s peak of gas phase molecular oxygen shifts toward low BE (red dash arrow). At 295 K, two peaks for O 1s appear at 538.3 and 539.3 eV, which are typical for O₂. Molecular oxygen has two configurations and photoionization of 1s core level leads to two multiplet states of ⁴Σ⁻ and ²Σ⁻ symmetry with different energies.⁴³ The peaks broadened, and shifted to 537.9 eV at 400 K, and to 537.6 eV at 450–500 K. It is also to be noted that the doublet observed for O₂ up to 350 K, changed to a featureless single broad peak at ≥ 400 K. Similar BE shift observed for vibration feature in NAP-UPS and core level of gas-phase O₂ attest the heterogeneity of the surface. While Ag 3d core level does not show any change in the presence of oxygen between 295 and 500 K (Figure S6), O atoms chemisorbed on the surface gives a broad peak around 530 eV, which can be deconvoluted to three components at 529.4, 530.3 and 531.1 eV. First two components at 529.4 and 530.3 eV are attributed to the nucleophilic and electrophilic O-atoms chemisorbed on the Ag-surface, respectively. This is in accordance to the earlier literature reports.^{10,12,42} High BE electrophilic oxygen indicates a relatively low negative charge on it and electron-rich alkenes are attracted towards this. Electrophilic oxygen is expected to be present on cationic Ag^{δ+} islands, which also makes the reaction with alkene easier. BE of both oxygen species shows the typical oxide (O²⁻) nature

Figure 6. O 1s spectra recorded on the silver surface at 0.2 mbar oxygen pressure between 295 and 500 K. Gas-phase oxygen features observed between 536–540 eV show a similar BE shift, as observed in NAP-UPS (Figure 2), indicating that the oxygen molecule can be used as probe molecules to observe the change in surface potential.

and supports the metal-oxide pair formation. It is also to be noted that there is no superoxo/peroxo type species are present on the silver surface and no feature observed between 532 and 533 eV supports this. The component at 531.1 eV is attributed to O atoms associated with defect sites as well as possible hydroxyl groups, due to interaction with residual hydrogen in the chamber. When the temperature is raised to 350 K, the relative amount of electrophilic oxygen also increases. With further increase in temperature, the overall intensity at 530 eV decreases, and a new peak appears at 528.7 eV. This new peak is attributed to subsurface oxygen in Ag. The lowest BE of O 1s for subsurface oxygen among the three components indicates the electron donation by adjacent Ag atoms. The lowest BE for subsurface oxygen suggests the oxide nature of subsurface oxygen. In fact, this induces marginally cationic character of the Ag surface. We correlate the diffusion of O into the subsurface with the change in WF. In addition, the space charge layer, created on the Ag surface, is likely to hinder the O₂ approaching the surface and this leads to a decrease in surface θ_{O} . We consider that this is crucial for the onset of attractive interaction with alkenes and subsequently to epoxidation.

On further increasing the temperature to 450 K, surface oxygen content increases again, while subsurface oxygen was still observed (Figure 6). Electrophilic oxygen at 530.3 eV increases more than other O-species. We attribute that electrophilic oxygen adheres to only

Figure 7. Angle-dependent O 1s spectra recorded under relevant conditions. Measurement at 430 K was made at the beginning of oxygen evacuation.

those surface atoms beneath which subsurface O atoms are present. Surface defects, which are present in large numbers on polycrystalline Ag, can facilitate the diffusion of subsurface oxygen as in the case of Pd.⁴⁴ It is to be noted that nucleophilic oxygen is also present on the surface, and they can simply combust alkene molecules. At 500 K, the intensity of the subsurface O 1s decreases while the nucleophilic and electrophilic oxygen nature changes and shifts to high BE at 529.7 and 530.6 eV, respectively. The intensity of the two components also grows in intensity. This indicates that silver surface is now covered with more oxygen than ≤ 450 K. This is attributed to the growth of surface oxide, begins above 450 K, and spreads to the immediate sub-surface layers. Consecutive changes in the WF of Ag indicate that the surface nature changes, which in turn supports the growth of oxide layers.

Diffusion of oxygen into sub-surfaces was further confirmed by angle-dependent O 1s studies and the results are shown in Figure 7, and peak fitting parameters are given in Table S1 in Supplementary Information (SI). Development of a new peak at 528.7 eV for subsurface oxygen is evident at 410 K (orange colour component) in the presence of 0.1 mbar O₂ at the normal emission of photoelectrons. However, under the above conditions, angle-dependent XPS shows decreasing subsurface oxygen intensity at lower angles, and

a simultaneous increase in electrophilic oxygen. This observation fully supports the presence of subsurface oxygen within the probing depth of XPS. Even at the beginning of evacuation of gas-phase oxygen, the surface nature changes considerably at 430 K. With increasing time in UHV or at high temperatures in UHV, the surface reverts to metal. A simple heating to 550 K for 2 min removes all the oxygen atoms present on the surface is shown in the top spectrum in Figure 7.

From the results, we conclude that oxygen diffusion occurs into the sub-surfaces and it affects Ag surfaces in two ways. Figure S7 represents the effects of subsurface oxygen in a schematic way. The population of oxygen in the sub-surfaces of Ag imparts a cationic character to the surface. As an electron-rich molecule, the sticking probability of ethylene to this modified Ag surface is likely to be higher than to metallic Ag. The surface silver atoms, which are coordinated to the subsurface oxygen, behave differently from those which do not have subsurface oxygen in their coordination. The former induces electrophilic nature in the oxygen adsorbed onto it. We speculate that the electrophilic oxygen activates ethylene to form EtO. The formation of space charge layers on modified Ag restricts oxygen but favours ethylene adsorption. With the increase in oxygen population in the sub-surface, the surface starts to oxidize gradually and at a certain extent forms the metastable surface oxide. It is to be reminded that commercial Ag-based catalysts work continuously at high pressures, and silver oxide is not active for epoxidation catalysis. A combination of the above facts with our observations suggests a subtle to moderate changes on silver surfaces under actual catalysis conditions.

4. Conclusions

Ethylene oxide is known to be thermodynamically unstable and it is more prone to combustion than ethylene under typical reaction conditions of epoxidation. We studied the changes in Ag over the temperature range which is actually employed in ethylene epoxidation. Oxygen diffusion into the subsurfaces of Ag predominantly occurs between 390 and 450 K, and due to this subsurface population, the Ag surface turns to marginally cationic in nature. The oxygen, further adsorbed on such a cationic Ag-surface, is electrophilic and is highly reactive to ethylene to form epoxide. The increase in work function of marginally oxidized silver, in the presence of O₂ at 400 K, compared to its metallic counterpart, fully supports the change in electronic nature of the Ag surface. In a very similar manner, the work function increases again at and above 450 K,

which reflects the increase in the extent of oxidation. Dynamic and metastable oxide formation on silver surfaces above 450 K favours the complete combustion of alkene to CO₂. A plausible reaction mechanism can thus be proposed from the present findings.

Valence band measurements reveal important changes in the Ag surfaces while Ag 3d core level shows minimal or no change. However, O 1s core level spectra reflect many changes observed in the VB regime. It suggests that changes specifically related to the surface are notably important to understand the reactivity of Ag and oxygen. The behaviour of supported Ag-catalysts, employed in industrial epoxidation processes, strongly depends on the size of Schottky barriers and band offsets in the heterojunctions between Ag and the semiconducting/insulating support.^{45–48} The band offset between metal and the support is expected to be minimized due to the space charge formation on the Ag surfaces by subsurface diffusion of oxygen, and hence WF changes on Ag also to be minimized. Indeed, a nearly equal E_F or a minimum difference in E_F is expected between Ag and the support surfaces in the active temperature-window under reaction conditions. Besides that, the formation of space charge on Ag, likely, facilitates epoxidation by facilitating the attraction of alkene molecules toward the catalyst. However, the nature of oxygen on the Ag surface might remain as observed in the present manuscript. The second change in WF, observed above 450 K, helps the formation of surface oxides which causes complete combustion of ethylene. It is also to be noted that industrial epoxidation catalysts employ silver supported on alumina with promoters and few other ingredients at high pressures (10–30 bar). Hence, we suggest for detailed work function measurements on model surfaces⁴¹ as well as on industrial catalysts with Kelvin probe force microscopy under reaction conditions. This is expected to give more information about the formation of the space charge layer and the role of surface charge in the reaction.

Supplementary Information (SI)

Supplementary Information contains calculated difference spectrum (Figure S1), deconvoluted NAP-UPS spectra (Figure S2), Ag valence band spectra recorded at 0.2 mbar O₂ (Figure S3), a set of NAP-UPS recorded at 0.1 mbar/350 K followed by evacuation (Figure S4), temperature dependent gas-phase O₂ spectra (Figure S5), Ag 3d core-level spectra recorded at 0.2 mbar O₂ and different temperatures (Figure S6), proposed model for Ag + O₂ interaction (Figure S7), and peak-fitting parameters for Figure 6 (Table S1). Supplementary Information is available at www.ias.ac.in/chemsci.

Acknowledgements

MKG and KPR, and RJ are thankful to the UGC, New Delhi, and CSIR, New Delhi, respectively, for research fellowships. We thank SERB (SR/S1/PC-16/2012) and CSC-0404 for partial funding of this research project.

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