MECHANISM OF THE INTERACTION OF ETHYLENE WITH ATOMIC OXYGEN ON A SILVER SURFACE

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ABSTRACT: The combustion mechanism of ethylene by atomic oxygen on silver (110) was investigated with the modern tools of surface science. Ethylene was oxidatively dehydrogenated by the adsorbed atomic oxygens to surface hydroxide and a surface residue of carbon atoms. The surface hydroxide intermediates rapidly reacted to yield water and adsorbed atomic oxygen, and the carbon atoms were subsequently oxidized by atomic oxygen to carbon dioxide. This investigation revealed that partially oxygenated hydrocarbons were not formed on the catalyst surface during the combustion of ethylene by atomic oxygen.

1. INTRODUCTION

The oxidation of ethylene by a silver catalyst has been examined more extensively than any other catalytic oxidation reaction because of the industrial importance of this process. Much of this effort has gone into elucidating the mechanism of this reaction and the factors affecting selectivity. The central issues concerning the mechanism and selectivity of this reaction are the nature of the adsorbed oxygen species and their subsequent interactions with ethylene. Recent studies on the interaction of oxygen with silver revealed that both molecular and atomic oxygen exist on the surface of a silver catalyst.1-7) Kilty et al.1) have reviewed the available information regarding the oxidation of ethylene over silver and concluded that ethylene reacts selectively with surface molecular oxygen via an Eley-Rideal mechanism to yield ethylene oxide, and the oxygen atom produced in this step subsequently reacts with another ethylene molecule from the gas phase to give combustion products. No suggestions were offered by Kilty et al. concerning the nature of the surface intermediate formed when ethylene reacts with atomic oxygen or the subsequent combustion mechanism. The mechanism of ethylene combustion by atomic oxygen on silver is not certain, and on the basis of kinetic and adsorption data a number of mechanisms were proposed for the combustion reaction.[8-13] The proposed mechanisms are rather speculative in light of the limited data that was available to the investigators. However, all of the mechanisms for the combustion of ethylene by atomic oxygen on silver proposed the formation of various partially oxygenated hydrocarbons (H_2CO, CH_3CHO, CH_3COOH, and vinyl alcohol) as the precursors to complete combustion.

The uncertainty in the mechanism of ethylene combustion by atomic oxygen adsorbed on silver motivated the present study. The combustion of ethylene by atomic oxygen adsorbed on silver was investigated with the modern techniques of surface science since recent oxidation studies of Ag (110) samples demonstrated that only atomic oxygen was present on the silver surface at the low oxygen partial pressures employed in surface science experiments.[6,7] In addition the surface science approach permits elucidation of the fundamental surface processes that occur during this reaction. Thus, this model system was ideally suited for the study of the interaction of ethylene with atomic oxygen on silver without complications due to the simultaneous presence of molecularly adsorbed oxygen.

2. EXPERIMENTAL

The experiments were performed in a stainless steel ultrahigh vacuum (UHV) chamber possessing the capabilities to perform temperature programmed reaction spectroscopy (TPRS), Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS), and low energy electron diffraction (LEED). The Ag (110) sample (5N purity) was purchased from Materials Research Corporation, and mounted on a tantalum foil. After several argon bombardment and annealing cycles a sharp LEED pattern and a clean AES spectrum resulted. The sample could be cooled to 150K, and a linear heating rate of ~10K/sec was typically employed in the TPRS experiments. Ethylene (research grade) was adsorbed on the partially oxidized silver surface from the background, but it was found necessary to introduce oxygen (research grade) through a doser arrangement due to the low sticking probability of oxygen on the clean silver surface.[6] A base pressure of about 1×10^{-10} Torr was routinely achieved, and most of the residual gas was helium from the UPS resonance lamp. Additional information about this UHV system can be found in previous publications.[14,15]

3. RESULTS

3.1. Interaction of Oxygen with Ag (110)

The interaction of oxygen with Ag (110), at room temperature and at low oxygen partial pressures, was extensively examined in recent years6,7) and was only briefly examined in the present investigation to ascertain that the results previously reported could be reproduced in the present system. The present oxygen - Ag (110) studies demonstrated that the LEED, UPS, TPRS, and AES results previously reported for this system could be reproduced.6,7,16) The oxygen uptake was determined by temperature programming the silver sample and monitoring the amount desorbed. Oxygen dissociatively adsorbed on the Ag (110) surface under the present experimental conditions, and $^{18}O_2$ and $^{16}O_2$ readily exchanged on the silver surface to yield $^{18}O^{16}O$. These experiments verified that only the atomic form of oxygen was present on the silver surface under the present experimental conditions.

3.2. Interaction of Ethylene with Ag (110)

Very little ethylene (<1% of a monolayer) adsorbed on the clean, oxygen-free Ag (110) surface at room temperature and above as determined by UPS and temperature programmed experiments. However, when the silver sample was cooled to ~150K about a monolayer of ethylene adsorbed on this surface. The UPS spectrum indicated that ethylene was molecularly adsorbed and primarily interacted with the silver substrate via its π orbital.17) LEED experiments of the adsorbed ethylene did not exhibit ordering of the adsorbate. Temperature programmed experiments revealed that ethylene was the only species to desorb from this surface, and the desorption occurred at ~200K. Thus, these experiments revealed that ethylene essentially does not adsorb on a clean Ag (110) surface at temperatures exceeding 200K, and at lower temperatures ethylene molecularly adsorbs on this substrate in a weakly bound state.

3.3. Interaction of Ethylene with Atomic Oxygen Adsorbed on Ag(110)

Temperature programmed reaction spectroscopy experiments showed that H_2O, CO_2, and O_2 were the only reaction products formed subsequent to the adsorption of ethylene on a (2 x 1) oxygen atom covered Ag (110) surface. Partially oxygenated hydrocarbons (H_2CO, CH_3CHO, etc.) were not observed. Water was not observed to desorb from the silver sample when the TPRS experiments were performed at room temperature, but substantial amounts of water evolved from the sample when the experiments were repeated at low adsorption temperatures (the oxygen was always adsorbed at room temperature). The details of water production were studied in greater detail with UPS, and these results will be discussed later in this paper. The evolution of CO_2 and O_2 subsequent to the ethylene-atomic oxygen interaction at room temperature are presented in Figures 1 and 2 as a function of ethylene exposure, respectively. Carbon dioxide was produced in the temperature range 400-525K, and its spectra are rather complex exhibiting several peaks that changed position with ethylene exposure. The CO_2 production initially increased with ethylene exposure, but at 40L (a Langmuir equals 10^{-6} Torr-sec.) exposure of ethylene almost no CO_2 was formed. The oxygen evolution shown in Figure 2 represents the recombination of oxygen atoms that were not consumed in the oxidation of ethylene over silver. The oxygen production continuously decreased with increasing ethylene exposure, and at 40L exposure of ethylene all of the oxygen atoms were consumed in the oxidation of ethylene. A comparison of the carbon dioxide and oxygen spectra suggests that CO_2 was produced at low ethylene exposures because excess oxygen was present on the surface subsequent to the formation of water; at 40L ethylene exposure almost all of the oxygen was consumed in the production of water and excess oxygen was not available for CO_2 production. This analysis implies that only carbon remained on the silver surface subsequent to a large exposure of ethylene at room temperature.

The sole presence of carbon on the Ag (110) surface subsequent to a large exposure of ethylene to an oxidized silver surface at room temperature was verified by AES, UPS, and TPRS experiments. The AES analysis was obtained as direct energy distributions N(E) because of the overlap of the intense silver Auger peaks with the carbon Auger peaks. The details of this procedure are presented elsewhere.[18)] AES analysis revealed that oxygen was not present on such a pretreated surface, and that only carbon was present on the silver surface. The AES analysis also revealed that the carbon Auger transitions were characteristic of a metal carbide surface

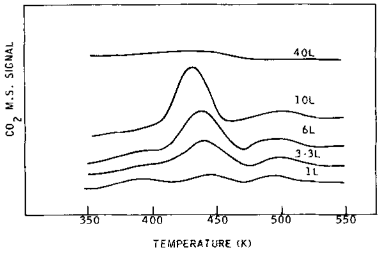

Fig. 1. CO_2 production from C_2H_4 adsorption on Ag (110)-(2 x 1)O.

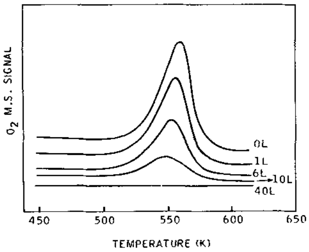

Fig. 2. O_2 production from C_2H_4 adsorption on Ag (110)-(2 x 1)O.

layer.[19)] The UPS difference spectrum of the silver carbide surface layer did not possess the characteristics associated with surface oxygen or adsorbed ethylene molecules. The AES and UPS spectra showed that the silver surface carbide transformed to another form of surface carbon when the sample was heated to temperatures exceeding 425K. The AES data also showed that the surface carbon did not diffuse into the bulk of the silver sample at elevated temperatures. LEED analysis of the Ag (110) surface carbide did not reveal an ordered structure. The presence of the surface carbon overlayer was further substantiated by its combustion to CO_2 in TPRS experiments. The reaction order of the combustion step was greater than unity because the CO_2 peak maxima shifted to higher temperatures with decreasing carbon coverage in the TPRS experiments. In these experiments water and hydrogen were not observed as reaction products; providing further evidence that hydrogen atom containing species were absent from the surface carbon layer.

The carbide Auger line shape of the surface carbon, formed by the dehydrogenation of ethylene by atomic oxygen on silver at room temperature, indicated that dissociated carbon atoms and not carbon dimers were present on the silver surface. Recent Auger studies demonstrated that changes in the carbon line shape coincide with changes in bonding or different chemical environments, and that the Auger peak shape can be used as a fingerprint to characterize the nature of the surface carbon.[20-22)] In these studies the carbide line shape was only observed when CO or C_2H_4 were completely dissociated on the metal surfaces.[21-22)] Further identification of the nature of the surface carbon was achieved through comparison of its combustion characteristics to that of carbon atoms on the silver surface produced by the disproportionation of a molecule containing only one carbon. The surface carbon atoms were deposited on the Ag (110) surface by sputtering in an ambient of either CH_4 or CO. The combustion characteristics of the surface carbon atoms in the TPRS experiments were similar to that previously found for the surface carbon produced from ethylene. Thus, these results indicate that the surface carbon produced from the interaction of ethylene with atomic oxygen on silver exists as individual carbon atoms.

The influence of the oxygen atom coverage on the Ag (110) surface upon the production of surface carbon from large ethylene exposures at room temperature was also examined. The total amount of carbon present on the Ag (110) surface was determined by oxidizing the carbon to CO_2 in a temperature programmed experiment.

The amount of surface carbon formed on the Ag (110) sample was found to be linearly dependent on the initial coverage of oxygen atoms. It also follows from this observation that at room temperature the oxygen atoms on the silver surface ($0<\theta\leq 1/2$) were selectively reacted by the hydrogens initially present in ethylene since CO_2 was not produced and H_2O was produced under these experimental conditions of excess ethylene.

Ultraviolet photoelectron spectroscopy studies were also undertaken to elucidate the initial interaction occurring from the adsorption of ethylene on an oxygen atom covered Ag (110) surface. The UPS ΔN(E) spectra that resulted from the adsorption of ethylene, 20L exposure, on a (2 x 1) oxygen atom covered Ag (110) surface at 160K and subsequent heating are presented in Figure 3. Comparable results were also obtained with a 2L exposure since the sticking probability of ethylene onto the oxygenated surface was very high at these low temperatures. In this series of spectra the oxygen was adsorbed at room temperature, the sample was cooled to 160K and exposed to ethylene, and the changes in the UPS difference spectra produced by heating the sample to various temperatures were monitored. The 160K spectrum was the simple sum of atomic oxygen and adsorbed ethylene, and could be reproduced from the individual results obtained for adsorbed oxygen atoms and ethylene respectively. The 175K spectrum was the sum of surface hydroxide and adsorbed carbon. The UPS and surface chemistry of surface hydroxide were also investigated and will be reported in a subsequent communication.[23] Upon further heating the sample to 235K the -11.0eV and -8.5eV peaks (associated with surface hydroxide) were substantially reduced and the -3.5eV peak (observed for a number of adsorbates) was decreased to half its original intensity. It was in this temperature interval that most of the water was observed to desorb from the sample in the temperature programmed experiments subsequent to the adsorption of ethylene on an oxygen atom covered silver surface. The UPS spectral features did not change upon heating the sample to 350K. Further heating of the sample to 475K resulted in the complete disappearance of the -8.5eV peak, substantial reduction of the -3.5eV peak, and a shift of the -5.2eV peak upward to -4.9eV. The parallel AES

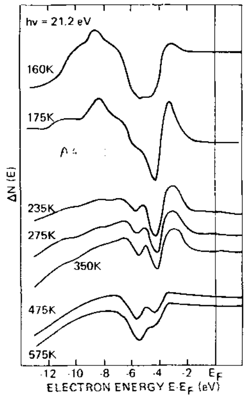

Fig. 3. UPS of C_2H_4 adsorption on Ag (110)-(2 x 1)O

and TPRS experiments showed that in this temperature range CO_2 was evolved from the sample, and the surface carbon transformed from a sharp carbide structure to a carbon envelope of peaks showing less distinctive features. Upon heating to 575K the peak present over the d emission shifted to higher energies and became less pronounced. The trends observed in the UPS experiments of the ethylene-atomic oxygen reaction over silver were in agreement with the observations made in the TPRS and AES experiments, and revealed that the initial interaction of ethylene with atomic oxygen on silver resulted in adsorbed hydroxide and adsorbed carbon atoms.

4. DISCUSSION

The oxygen-Ag (110) studies demonstrated that results previously reported in the literature for this system could be reproduced, and that only the atomic form of oxygen was present on the silver surface under the present experimental conditions.

The ethylene-silver interaction was very weak and ethylene did not adsorb on the clean Ag (110) surface at temperatures exceeding 200K. The ethylene-silver interaction has not received much attention in the catalysis literature, but several investigators did demonstrate that a completely reduced silver surface does not adsorb ethylene at temperatures employed for ethylene oxidation.24)

Ethylene readily adsorbed on a silver surface containing oxygen atoms at room temperature, and the ethylene uptake was directly proportional to the surface coverage of oxygen atoms. Thus, oxygen atoms provide active sites for ethylene combustion since only CO_2 and H_2O were produced. The initial interaction between ethylene and adsorbed atomic oxygen led to the formation of surface hydroxide and surface carbon; this reaction was extremely rapid since hydroxide was produced at temperatures less than 175K. An attempt was made to isolate C_2H_x intermediates potentially present during the oxidative dehydrogenation of ethylene by adsorbing an excess of ethylene on a silver surface only partially covered with oxygen atoms, but such an intermediate was not observed with UPS. The surface carbon produced from this reaction existed as individual carbon atoms. The surface hydroxide intermediates reacted to yield water and adsorbed atomic oxygen; this reaction was also very rapid since most of the water was produced at temperatures less than 235K. The surface carbon atoms produced from the interaction of ethylene and atomic oxygen on silver were subsequently oxidized to carbon dioxide by surface oxygen atoms, but this reaction was much slower and only occurred at temperatures exceeding ~400K.

Additional experiments with surface hydroxide on Ag (110) revealed that ethylene was not oxidized by the hydroxide intermediate.23) These results indicate the following mechanism occurs during the combustion of ethylene by atomic oxygen on silver:

$$C_2H_4 + O_{ads} \xrightarrow{3O_{ads}} 2C_{ads} + 4OH_{ads} \qquad (1)$$

$$OH_{ads} + OH_{ads} \longrightarrow H_2O + O_{ads} \qquad (2)$$

$$C_{ads} + 2O_{ads} \longrightarrow CO_2 \qquad (3)$$

The formation of surface carbon and hydroxide, reaction step (1), is not an elementary step and consists of several rapid steps in series. The details of these steps are not known because the oxidative dehydrogenation of ethylene was extremely fast. The efficiency of the oxidative dehydrogenation of ethylene accounts for the absence of hydrogen redistribution when mixtures of C_2H_4 and C_2D_4 were oxidized over silver.25) The UPS experiments demonstrated that at low temperatures the combustion of ethylene by atomic oxygen, reaction step (1), proceded with ethylene adsorbed on the silver surface. This ethylene combustion pathway was previously proposed by Force and Bell24) but it still is not clear if above room temperature this reaction competes with the direct adsorption of ethylene from the gas phase onto adsorbed atomic oxygen. The reaction of surface hydroxide to water and oxygen atoms, reaction step (2), is an elementary step and regenerates the active oxygen atoms necessary for ethylene combustion. The low reactivity between ethylene and the hydroxide intermediate suggests that the presence of surface hydroxide should decrease the rate of ethylene oxidation over silver catalysts. Metcalf and Harriott examined the effect of water on the oxidation of ethylene over silver and found that the rate of ethylene oxidation declined with the addition of water.26) The formation of carbon dioxide, reaction step (3), must also be an elementary step since carbon monoxide was not produced and carbon dioxide production exhibited kinetics associated with nonlinear reactions. The excess oxygen atoms retained on the silver surface after the combustion of surface carbon recombined and desorbed from the surface as O_2 at ~560K. The ethylene combustion experiments also demonstrated that on the silver surface oxygen atom combustion of ethylene was a more rapid reaction process than the recombination of oxygen atoms.

Partially oxygenated hydrocarbons were not formed during the combustion of ethylene by adsorbed atomic oxygen on silver. Partially oxygenated hydrocarbon intermediates form very stable surface complexes on silver and several species were isolated in previous oxidation studies.[1,24,27-31] Surface alkoxides, CH_3O_{ads} and $CH_3CH_2O_{ads}$, were formed during the oxidation of CH_3OH and CH_3CH_2OH over silver, respectively.[27,28] Surface silver formates, $HCOO_{ads}$, were produced during H_2CO and HCOOH oxidation,[29,30] and surface acetates, CH_3COO_{ads}, were produced during CH_3CHO and CH_3COOH oxidation over silver.[31] The characteristics of these partially oxygenated hydrocarbon intermediates are well documented and they would have been readily identified if they were present during ethylene combustion by atomic oxygen over silver. The mechanisms previously proposed for the combustion of ethylene by atomic oxygen on silver were based on kinetic and adsorption data and, with the exception of Force and Bell's study,[12,24] no direct evidence was available for the formation of partially oxygenated hydrocarbons from ethylene combustion. The trace amount of acetaldehyde produced during ethylene oxidation over supported silver catalysts is probably due to the gas-phase and/or heterogeneous isomerization of ethylene oxide to acetaldehyde.[11,32,33] Force and Bell obtained the infrared spectra of the adsorbed species present during the oxidation of ethylene over silver and observed features in their spectra which they attributed to adsorbed acetaldehyde. From this observation they postulated the mechanism of ethylene combustion over silver. Force and Bell's investigations were complicated by the presence of several different oxygen species on the silver surface, and ethylene oxide and carbon dioxide in the gas phase. The source of their adsorbed acetaldehyde is not unambiguous. In the present investigation only ethylene was adsorbed onto the atomic oxygen covered Ag (110) surface, and partially oxygenated hydrocarbons were not observed.

5. CONCLUSION

The combustion of ethylene by atomic oxygen on Ag (110) was investigated with the modern tools of surface science. Ethylene was oxidatively dehydrogenated by the adsorbed atomic oxygen to surface hydroxide and a surface residue of carbon atoms. The surface hydroxide intermediates rapidly reacted to yield water and adsorbed atomic oxygen, and the carbon atoms were subsequently oxidized by atomic oxygen to carbon dioxide. This investigation revealed that partially oxygenated hydrocarbons were not formed on the silver surface during the combustion of ethylene by atomic oxygen.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the stimulating discussions with T. Fischer, A. Kaldor, R. Polizzotti, and J. Sobel through various stages of this work.

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DISCUSSION

S. Tanaka (Senshu Univ., Kawasaki)

1) In Fig. 1, we can see several CO_2 peaks that changed position with ethylene exposure. How do you explain these several peaks?

2) I would like to know the difference between silver surface carbide and other forms of surface carbon in reactivity with oxygen, as well as other characteristics.

3) Have you checked the silver catalyst surface by Auger electron spectroscopy after the ethylene oxydation reaction proceeded under normal reaction conditions?

I.E. Wachs

The presence of several CO_2 TPRS peaks from the combustion of ethylene on Ag(110) most probably suggests that carbon, the precursor to CO_2 production, is distributed inhomogeneously over the silver surface. At conditions where the production of CO_2 was large only one CO_2 TPRS peak was observed to dominate the spectrum.

AES experiments showed that carbon was present on silver as a carbide structure below 425K, and exposure to higher temperatures resulted in the loss of the sharp fine structure associated with the carbide but the total carbon signal remained constant in intensity. Parallel UPS measurements also exhibited major changes in the valence band region accompanying the Auger line shape change. The reactivities of carbon produced at room temperature and carbon heated to high temperatures towards adsorbed oxygen atoms on Ag(110) were found to be similiar as judged by the CO_2 production in TPRS experiments.

We have examined the surfaces of unsupported silver powders employed in ethylene oxidation under normal reaction conditions with Auger electron spectroscopy, and find that under certain conditions carbon is present on the catalyst surface.[1]

M. Egashira (Nagasaki Univ.)

1) Is the adsorbed atomic oxygen species negatively charged or neutral?

2) How many peaks were observed in the thermal desorption of the surface hydroxyl groups as water, and at what temperatures?

I.E. Wachs

Engelhardt and Menzel calculated the charge transfer to the adsorbed oxygen atoms on Ag(110) from work function measurements, and estimated a charge transfer of between 0.08 and 0.18 of an electronic charge.[2] In the present investigation the work function changes due to the adsorption of oxygen atoms on

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1) I.E. Wachs, C.C. Chersich, and S. Behal, unpublished results.

2) H.A. Engelhardt and D. Menzel, Surface Sci., 57, 591 (1976).

Ag(110) were obtained by measuring the low energy cut off of the secondary emission in the photoelectron energy distributions, and the results are in agreement with Engelhardt and Menzel's conclusions.

The thermal desorption of surface hydroxide from Ag(110) yielded a complex desorption spectrum with a maximum at approximately 235K.

S. Kagawa (Nagasaki Univ.)

It is well known that catalytic properties of silver change with its oxidation state. For example, the conversion of ethylene and the selectivity to ethylene oxide depend on the oxidation state of the silver surface. Recently, Kuczkowski and co-workers found that upon epoxidation of ethylene the rotation around the C-C bond of ethylene is not perfectly free, but is restricted depending on the oxidation state of silver surface. In the commercial process, the reaction gas contains a considerable amount of excess oxygen. However, your experimental conditions were very different from this. You observed atomic carbon only on the oxygen-free silver surface. I wonder whether the combustion mechanism obtained from such a conditions is the same as that occurring in the commercial process. I would like to know your opinion about this point.

I.E. Wachs

The objective of the present investigation was to determine the mechanism of ethylene combustion by atomic oxygen on silver. Several investigators have demonstrated that at low partial pressures of oxygen only adsorbed oxygen atoms are present on the silver surface.[2-4] Thus, this model system, oxygen atoms adsorbed on Ag(110), was ideally suited for the study of the interaction of ethylene with atomic oxygen on silver without complications due to the simultaneous presence of molecularly adsorbed oxygen.

Rovida and Pratesi[3,4] investigated the adsorption of oxygen on Ag(110) at oxygen pressures up to 1 Torr and found that at maximum oxygen coverage a (2 × 1) LEED super structure is obtained. Although the present investigation employed oxygen partial pressures of $\sim 10^{-6}$ Torr the same maximum coverage of adsorbed oxygen atoms was obtained. This suggests that the

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3) G. Rovida and F. Pratesi, Surface Sci., 52, 542 (1975).
4) G. Rovida, J. Phys. Chem., 80, 150 (1976).

ethylene combustion mechanism observed in our study is applicable over many orders of oxygen partial pressures. The available information about ethylene oxidation over silver at higher pressures does not contradict the ethylene combustion mechanism presented here. Future fundamental research will extend this reaction to higher partial pressures of oxygen and determine if the ethylene combustion mechanism outlined in this paper is also operative under these conditions.

Ethylene oxide is produced commercially via two different technologies: air-based and oxygen-based. Only the oxygen-based process employs excess oxygen.

M.M. Bhasin (Union Carbide, South Charleston)

In Fig. 3 of the manuscript ultraviolet exposure (under UPS measurements) time is perfectly correlated with temperature. Did you sort out the effects of these variables – in other words, what happens when the ultraviolet exposure is prolonged to the extent employed in your experiments?

1) When you oxidized residual carbon (after the ethylene-oxygen interaction experiment) from Ag(110), was the (110) structure maintained?

2) On page 5 of the manuscript you state "The AES data also showed the surface carbon did not diffuse into the bulk of the silver sample at elevated temperatures." Would you describe the AES data obtained to support this.

3) Have you tried this reaction with other silver surfaces, particularly (111)?

I.E. Wachs

The UPS results presented in Fig. 3 were only dependent on temperature and independent of time. The UPS spectra were not found to alter from ultraviolet exposure of about 45 minutes which corresponded to the length of the experiment.

No reconstruction of the Ag(110) surface was observed in the present investigation, but during the combustion TPRS experiments the silver sample was heated to temperatures as high as 650K. These high temperatures may have annealed out potential structural changes.

The surface carbide Auger line shape was maintained upon heating to 425K. At higher temperatures the fine structure associated with the carbide was lost, but the total integrated AES carbon signal remained constant in intensity. From this observation it was concluded that diffusion of carbon into the bulk of the silver sample did not occur since the total amount of carbon in the surface region of the silver sample remained constant.

The oxidation of ethylene by atomic was only investigated on Ag(110) since the O_2-Ag interaction on this plane has been extensively characterized in the literature.[2-4]

Y. Takasu (Yamaguchi Univ.)

You have written in your text that none of the partially oxygenated hydrocarbons were observed. I also think that ethylene could be decomposed to form carbon and hydroxide by the adsorbed oxygen on the surface; however, I fear that the decomposition of ethylene should be complete between 175 and 350K. Induced levels based on adsorbed ethylene on various metal surfaces appear between 6 and 10 eV and around 5 eV. You write that both peaks at 8.5 and 11 eV could be assigned to hydroxide. Do you also assign the shoulder or peak around 6.5 eV to hydroxide or deposited carbon? Also, could you show me the UPS spectrum of the hydroxide on silver?

I.E. Wachs

The UPS He (I) spectra of the adsorbed atomic oxygen, carbon, hydroxide, and ethylene on Ag(110) are presented below. Note that all of these spectra are sufficiently distinct to allow direct identification of these species from their UPS spectra. All of the adsorbates on Ag(110) exhibit a peak at -3.5 eV. The UPS of adsorbed ethylene has peaks at -5.2 eV, -7 eV, -9 eV, and -10.2 eV which demonstrate that ethylene is molecularly adsorbed. This spectrum indicates that the ethylene molecule primarily interacts with the silver substrate via its π orbital, and remains undistorted. The surface hydroxide exhibits only two UPS peaks occurring at -8.2 eV and -11.0 eV in agreement with OH_{ads} on platinum.[5] The UPS of adsorbed carbon, in the carbide form, and adsorbed atomic oxygen do not posses well defined features below -6.0 eV, and can readily be distinguished from OH_{ads} and C_2H_{4ads}. The carbon can most notably be distinguished from the atomic oxygen by the double minimum in the carbon UPS spectrum occurring between -4.0 eV and -7.0 eV. From these spectra we conclude that the shoulder observed around -6.5 eV in the UPS of Fig. 3 is due to the presence of adsorbed carbon. The different UPS features exhibited by

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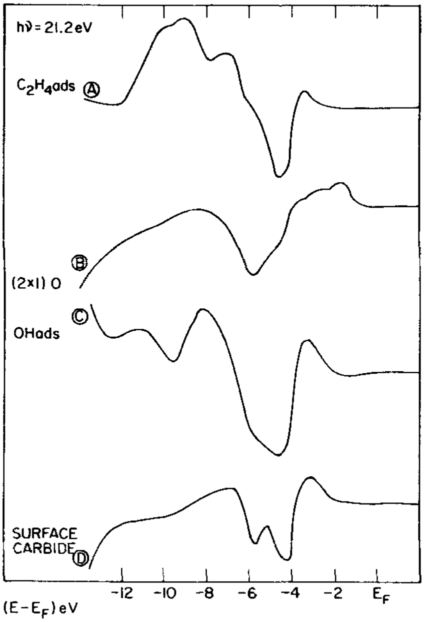
5) G.B. Fisher and B.A. Sexton, Phys. Rev. Lett., 44, 683 (1980).

the adsorbed species on Ag(110) allowed for their clear identification during ethylene combustion by atomic oxygen.



UPS of adsorbed species on Ag(110): A-C_2H_4 B-(2× 1)O atomic oxygen C- hydroxide produced from adsorption of H_2O on (2 × 1)O at 200K D- surface carbide produced from adsorption of C_2H_4 on (2 × 1)O surface at 300K.

W.M.H. Sachtler (Koninklijke/Shell-Lab., Amsterdam)

Dr. C. Backx in our lab. has recently studied the interactions of Ag(110) with O_2 and C_2H_4 using techniques including Electron Energy Loss Spectroscopy. He found that adsorbed oxygen increases the adsorption of C_2H_4 by e.g. a factor of 13. The ethylene is adsorbed with the C-C axis parallel to the surface. Exposing adsorbed oxygen to gaseous C_2H_4 resulted in a surface carbonate only at very high exposures ($\sim 6x10^4$L).

As he did not observe the adsorbed carbon which you have found by UPS, I wonder whether these C atoms are located in interstices below the surface and undetectable by ELS.

I.E. Wachs

During ethylene combustion by atomic oxygen adsorbed on Ag(110) carbon deposition was only observed for temperatures below about 125°C. At higher reaction temperatures a "clean off" reaction occurred and the carbon was combusted to CO_2. The presence of carbon on the silver sample was verified directly by AES and UPS, and could subsequently be combusted in TPRS experiments to CO_2. Although these techniques are surface sensitive they do not distinguish between the topmost surface layer and the first few subsurface layers. In order to determine the location of the carbon on Ag(110), whether surface or subsurface, it is necessary to employ other techniques such as low energy ion scattering.

In addition to the adsorbed oxygen atoms on Ag(110) subsurface oxygen atoms were also found to be present. The presence of the subsurface oxygen was determined with oxygen isotopic labeling experiments. Adsorption of 99% $^{18}O_2$ on Ag(110) yielded substantial quantities of $^{16}O_2$ and $^{16}O^{18}O$ in the subsequent TPRS experiments, and the ratio of the oxygen isotopes depended on O_2-Ag(110) history. In the absence of adsorbed oxygen atoms the subsurface oxygen did not adsorb C_2H_4 or CO_2 on Ag(110) at 300K. During ethylene combustion by $^{18}O_2$ substantial quantities of $C^{16}O^{18}O$ and $C^{16}O^{16}O$ were observed revealing that the subsurface oxygen participated in the combustion reaction through exchange with surface ^{18}O.

A third state of oxygen on Ag(110) was also found in this study. Adsorption of O_2 at about 150K produced a new low temperature binding state at $\sim$230K for oxygen desorption in the TPRS experiments. This oxygen state exhibited first order desorption and did not undergo $^{18}O_2$ and $^{16}O_2$ exchange. From these observations it was concluded that this state corresponded to molecularly adsorbed oxygen on Ag(110).