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The Interaction of Ethylene with Surface Carbonate and Hydroxide Intermediates on Silver

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The surface chemistry of the intermediates formed from the adsorption of CO_2 and H_2O on an oxygen-atom-covered Ag(110) surface was investigated with surface spectroscopic techniques. Carbon dioxide complexed with adsorbed oxygen atoms to form a surface carbonate intermediate, and the associative adsorption of water led to the formation of surface hydroxides. CO_2 adsorption on the oxygen atom covered Ag(110) surface produced two-dimensional rearrangements of the surface species. Ethylene was not found to react with CO_{3ads} and OH_{ads} below room temperature, but did exhibit some reactivity toward CO_{3ads} at room temperature. This investigation showed that the formation of CO_{3ads} and OH_{ads} on the silver surface are responsible for the inhibiting effects of CO_2 and H_2O during ethylene oxidation over silver catalysts.

1. INTRODUCTION

The CO_2 and H_2O present during oxidation reactions over silver catalysts have been shown to influence the rates of reaction (*1*, *2*). The influence of carbon dioxide upon ethylene oxidation over silver catalysts in fixed-bed reactors was examined in several investigations (*1*). Hayes found that the addition of CO_2 during ethylene oxidation over silver catalysts promoted with calcium inhibited the production of C_2H_4O and had no effect on the production of carbon dioxide (*1*). Nault *et al.* observed that over silver supported on silicon carbide carbon dioxide strongly inhibited both the rates of CO_2 and C_2H_4O formation, and selectively suppressed the formation of C_2H_4O (*1*). Metcalf and Harriott employed silver supported on α-alumina and found that CO_2 addition inhibited both the rates of C_2H_4 and CO_2 production; the rate of CO_2 formation was suppressed to a greater extent than the rate of C_2H_4O formation to produce an increase in selectivity (*1*). Force and Bell also observed that the addition of CO_2 to ethylene oxidation over silver supported on Cab-O-Sil decreased the rates of C_2H_4O and CO_2 production, but both rates were equally inhibited in their study and no changes in the selectivity occurred. All of these investigations demonstrate that addition of CO_2 to ethylene oxidation over silver catalysts decreases the rate of ethylene oxidation, but there is no general agreement upon carbon dioxide's influence on the selectivity of this reaction. In the studies cited the ethylene oxide selectivity was observed to decrease, increase, and remain constant from the addition of carbon dioxide to the feed. These results suggest that carbon dioxide's influence upon the ethylene oxide selectivity may depend on the nature of the support and intentional and unintentional promoters present on the silver catalyst. No systematic studies appear to have been performed to isolate the various factors influencing the selectivity during the addition of CO_2 to ethylene oxidation over silver. The influence of H_2O upon ethylene oxidation over silver catalysts in fixed-bed reactors has not been examined as extensively as CO_2 addition. Hayes found that low partial pressures of H_2O had no apparent effect on the rate and selectivity of C_2H_4 oxidation over silver catalysts promoted with calcium (*1*). Metcalf and Harriott demonstrated that H_2O addition inhibited the rates of CO_2 and C_2H_4O production

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over silver-supported α-alumina catalysts; the two rates were equally suppressed so that no changes in ethylene oxide selectivity resulted (*1*).

These observations have led several investigators to examine the adsorption properties of CO_2 and H_2O on reduced and oxidized silver (*2–7*). Most workers did not detect chemisorption of carbon dioxide on reduced silver (*2–6*), but infrared spectral data under reaction conditions suggest the presence of adsorbed carbon dioxide on reduced silver (*7*). All investigators agree that carbon dioxide chemisorbs on oxidized silver in the form of a CO_3 surface intermediate (*2–7*). Czanderna used an ultramicrobalance to show that the quantity of carbon dioxide adsorbed is directly related to the number of adsorbed oxygen atoms on silver powder at temperatures below 375 K, and concluded that an adsorbed CO_3 complex was formed from this interaction (*4*). In subsequent thermal desorption studies Czanderna and Biegen demonstrated that CO_2 desorbed from an oxygen-covered silver surface via a first-order process (*5*). Additional evidence for the formation of the adsorbed carbonate on silver was obtained from oxygen isotope experiments. Keulks and Outlaw employed a recirculation reactor system to study the interaction of CO_2 with silver powder preadsorbed with oxygen-18 (*2*). In this investigation substantial amounts of $C^{16}O^{18}O$ and $C^{18}O_2$ were produced from $C^{16}O_2$ which implicated the formation of a CO_3 intermediate on the silver powder. Bowker *et al.* also examined the CO_2–O_2–Ag(110) system with oxygen-18 and temperature-programmed reaction spectroscopy (TPRS) (*6*). The desorption of CO_2 from the oxidized silver surface was found to be first order and substantial amounts of oxygen-18 were incorporated into the desorbed carbon dioxide. It was also concluded from this data that CO_{3ads} was formed on the silver surface. Studies of the adsorption of water on reduced and oxidized silver indicate that water does not chemisorb on reduced silver, but adsorbs on oxidized silver with the formation of OH surface intermediates (*1, 6, 8*). Hayes demonstrated that H_2O exchanges its oxygen with oxygen-18 from the silver catalyst under reaction conditions (*1*). Bowker *et al.* examined the H_2O–O_2–Ag(110) system with oxygen-18 and TPRS (*6*). The adsorption of water on the oxygen-18 atom covered silver surface at 160 K yielded a new binding state of H_2O in the TPRS experiments, and water desorbed as $H_2{}^{18}O$ and $H_2{}^{16}O$, while the oxygen primarily desorbed as $^{16}O_2$ and $^{16}O^{18}O$. The presence of OH intermediates on oxidized silver from the adsorption of water was inferred from these oxygen isotope experiments.

The present investigation was undertaken to obtain fundamental information about the properties of the CO_3 and OH intermediates adsorbed on silver. The CO_{3ads} and OH_{ads} present on Ag(110) were characterized with ultraviolet photoelectron spectroscopy, low-energy electron diffraction, and temperature-programmed reaction spectroscopy. The interaction of ethylene with these surface intermediates was also studied to elucidate some of the fundamental surface processes occurring during the oxidation of ethylene over silver, and to better understand the influence CO_2 and H_2O have upon this reaction.

2. EXPERIMENTAL

The experiments were conducted in a stainless-steel ultrahigh vacuum (UHV) chamber possessing the capability to perform temperature-programmed reaction spectroscopy (TPRS), Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS), and low-energy electron diffraction (LEED). A double-pass cylindrical mirror analyzer (Physical Electronics) was used for electron energy analysis in Auger and ultraviolet photoelectron spectroscopy. Auger electron spectra could be obtained either in the customary differentiated form dN/dE with the help of a phase-sensitive detector or as direct energy distributions $N(E)$, by electron counting with a Northern NS-575 multichannel analyzer. Surface structural information was obtained with a standard four-grid LEED system. An EAI quadrupole mass spectrometer system was used to monitor the gas composition in the UHV system during the TPRS experiments. The products observed in the TPRS experiments were identified by carefully comparing their observed cracking patterns in the mass spectrometer with those tabulated in the literature. The sample could be cooled to 150 K by circulating liquid nitrogen in a stainless-steel coil which supported the sample holder. Sample heating was achieved by electron bombardment from the rear, and a linear heating rate of ~10K/sec was typically employed in the TPRS experiments. The UHV system was pumped by ion and titanium sublimation pumps, and a base pressure of about 1×10^{-10} Torr was routinely achieved. Most of the residual gas was helium from the UPS resonance lamp. Additional information about this UHV system can be found in previous publications (*9*).

The work function, defined as the binding energy of electrons excited from the Fermi level, was obtained from the overall width ΔE of the UPS energy distribution (*10*):

$$\phi = h\nu - \Delta E + \tfrac{1}{2}\Delta E_{\mathrm{res}},$$

where ϕ is the work function, $h\nu$ the photon energy, ΔE the width measured from the energy at which the distribution at the Fermi edge has reached half its maximum height to the low-energy cutoff of the distribution, and ΔE_{res} is the energy broadening due to the finite resolution of the instrument. ΔE_{res} can be obtained by comparing the experimental shape of the Fermi edge with its theoretical value. The UPS spectra reported from this laboratory were collected with no bias voltage applied to the sample and with a 30° angle of incidence of the photon beam. Additional information regarding this procedure can be obtained in Evans' article (Ref. (*10*)).

The Ag(110) sample was purchased from Materials Research Corporation and was oriented within 0.5–1.0° of the (110) plane. The Ag(110) crystal had a purity of 99.999%. The silver sample was mounted on a tantalum foil. The initial Auger spectrum of the silver surface showed high concentrations of S, Cl, C, N, and O. These Auger peaks readily disappeared after several argon ion bombardment and annealing cycles. The sample was usually annealed at 800 K for several minutes resulting in a sharp (1 × 1) LEED pattern characteristic of the clean Ag(110) single-crystal surface. Routine sample cleaning was accomplished by oxygen adsorption at room temperature and subsequent heating to 800 K *in vacuo*. This procedure was effective for removal of carbon and minimized the need for argon sputter cleaning. However, Auger analysis of the silver surface revealed an increase of oxygen with time.

Oxygen (research grade) was introduced through a doser arrangement due to its low sticking coefficient on the clean silver surface (*11*, *12*). The doser supplied the front of the Ag(110) surface with an oxygen partial pressure that was substantially greater than the simultaneous oxygen background pressure. The oxygen uptake was readily determined by monitoring the amount of oxygen desorbed from temperature programming of the silver sample and the LEED patterns. With the present doser arrangement it required only approximately 10 system Langmuirs of oxygen exposure to achieve the (2 × 1) LEED pattern that corresponds to a half monolayer of oxygen atoms on Ag(110) (*11*). A Langmuir is defined as 10^{-6} Torr-sec of exposure; system Langmuir refers to the oxygen exposure measured in the background which is substantially less than the effective oxygen partial pressure supplied to the silver surface by the doser. It has been well documented that under the present experimental conditions, low partial pressures of oxygen and room temperature adsorption, only the atomic form of oxygen is present on the silver surface (*11–13*). Research grade ethylene, CO_2, and purified H_2O were adsorbed from the background because of their high adsorption efficiency on the partially oxidized silver surface.

3. RESULTS

A. Chemistry of Surface Carbonate

No evidence was found for chemisorption of carbon dioxide upon the oxygen-free Ag(110) surface at room temperature as determined from UPS and TPRS experiments. This is in sharp contrast to the adsorption and desorption of carbon dioxide from Ag(110) covered with atomic oxygen. Exposure of CO_2 to the silver surface precovered with atomic oxygen at room temperature resulted in the evolution of CO_2 and O_2 from the surface during subsequent TPRS experiments. The carbon dioxide temperature programmed spectra for a Ag(110) surface initially possessing a (4 × 1)O LEED pattern, corresponding to one-fourth monolayer of oxygen atoms, are presented in Fig. 1 as a function of CO_2 exposure. The oxygen atoms remaining on the silver surface after the evolution of CO_2 recombined and desorbed from the surface as O_2 at ~560 K. The desorption of CO_2 was a first-order process as evidenced by the invariance of the TPRS peak position with CO_2 exposure. The areas under the CO_2 TPRS spectra represent the CO_2 uptake, and the TPRS data were integrated and replotted in Fig. 2 to show the carbon dioxide uptake as a function of CO_2 exposure. The CO_2 mass spectrometer signal was previously calibrated for this system (*13*, *14*). These plots reveal that the carbon dioxide adsorption saturated when the CO_2/O ratio on the silver surface approached unity. The same results were also observed for a Ag(110) surface possessing a one-eighth monolayer of oxygen atoms as shown in Fig. 2. The first-order desorption of CO_2 from an oxygen atom covered silver surface and the saturation of the surface with CO_2 when the CO_2/O ratio approached unity support the formation of a surface intermediate having the stoichiometry CO_3:

$$CO_2 + O_{ads} \rightleftarrows CO_{3ads}. \qquad (1)$$

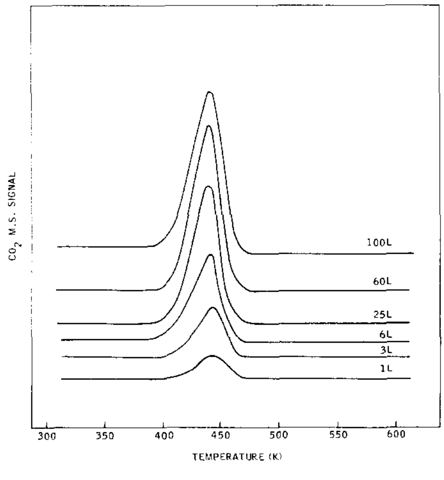

FIG. 1. CO_2 thermal desorption spectra from (4 × 1)O-covered Ag(110) as a function of CO_2 exposure.

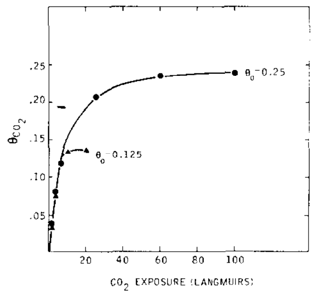

FIG. 2. CO_2 uptake on oxygen-atom-covered Ag(110) as a function of CO_2 exposure and preadsorbed oxygen.

The two-dimensional ordering of the CO_3 intermediate adsorbed on the Ag(110) surface was examined with low-energy electron diffraction. Saturation exposure of carbon dioxide to a (4 × 1) oxygen atom covered surface at room temperature produced a (2 × 2) LEED pattern. The (2 × 2)CO_3 pattern resulting from carbon dioxide adsorption on a (4 × 1)O covered surface can be interpreted as a restructuring of the two-dimensional network of the surface intermediates, and scattering from the presence of one quarter monolayer of surface carbonate. The (2 × 2) LEED pattern suggests that a carbonate intermediate is present in every other site along the channels of the Ag(110) surface as well as every other parallel channel. The carbonate LEED patterns were not stable to prolonged electron beam exposure. In the absence of the electron beam the (2 × 2)CO_3 LEED pattern was stable and could be observed after 45 min of its initial formation. In the presence of the electron beam the (2 × 2) pattern was converted to a (1 × 2) pattern in a few minutes. Following CO_2 adsorption on Ag(110) containing oxygen atom coverages less than (4 × 1)O only a (1 × 2) LEED pattern was observed. However, this pattern possessed considerable enlargement of the diffraction spots with increased background intensity. This indicates a breakdown in the registry of the scattering species with the substrate along the channels of the Ag(110) surface, but some degree of registry was maintained across the channels as evidenced by the presence of the enlarged fractional order spots. The LEED results demonstrate that complexing of the CO_2 with the oxygen atoms on Ag(110) induced rearrangement of the surface species.

The adsorbed CO_3 intermediate was also examined with ultraviolet photoemission spectroscopy. A comparison of the UPS Δ*N*(*E*) for adsorbed oxygen atoms, surface carbon (produced by the oxidative dehydrogenation of C_2H_4 (*13*)), and adsorbed carbonate are presented in Fig. 3. The adsorbed CO_3 exhibits electronic characteristics which are distinct from adsorbed oxygen or carbon. Most notable are the relatively sharp emission features at −3.3 and −8.5 eV for $CO_{3\text{ads}}$. These UPS features are sufficiently unique to surface carbonate that they can be used to indicate the presence of $CO_{3\text{ads}}$.

Work function changes due to the formation of the carbonate intermediate on the Ag(110) surface were obtained from the photoelectron energy distributions (*10*). The work function changes relative to the clean Ag(110) surface were obtained following a saturation exposure of CO_2 at room temperature to a silver surface preadsorbed with known quantities of atomic oxygen, and the Δϕ are presented in Fig. 4. The work function was found to increase linearly with the density of the adsorbed CO_3 species. From Fig. 4 a dipole moment of 0.57 Debye per adsorbed carbonate intermediate, independent of coverage, is obtained. This analysis interprets the increase in work function in terms of the formation of a dipole layer. Engelhardt and Menzel previously determined a dipole moment of 0.54 Debye per adsorbed oxygen atom on Ag(110) (*11*), and this implies similar

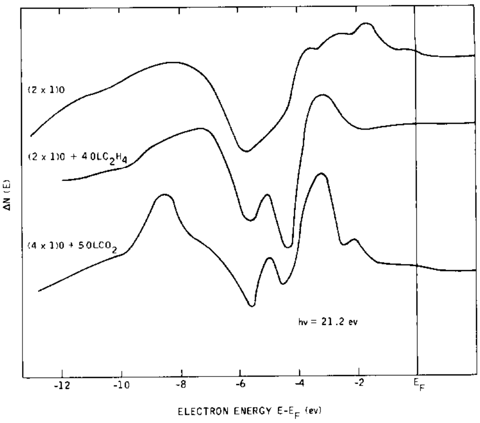

FIG. 3. Δ*N*(*E*) UPS of atomic oxygen, carbon, and carbonate adsorbed on Ag(110).

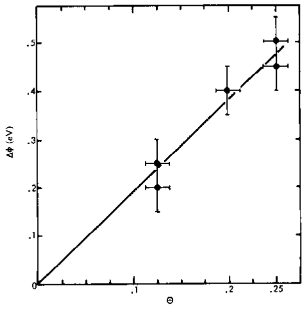

FIG. 4. Work function changes due to adsorbed carbonate on Ag(110) surface.

charge transfer per adsorbed species in both cases.

The interaction of ethylene with the surface carbonate intermediate was also investigated. Figure 5 shows that when the CO_{3ads} intermediate was exposed to 40 L of ethylene at room temperature the subsequent TPRS spectrum exhibited almost no CO_2 evolution. Simultaneous AES and UPS analysis of the silver surface revealed that only carbon was present on the Ag(110) surface. This surface carbon was subsequently combusted to CO_2 by adsorbing additional oxygen, and temperature programming the silver sample. The CO_2 TPRS spectra from these experiments agreed with results previously obtained for combustion of carbon from Ag(110) (*13*). To gain additional insight into this surface reaction $^{13}CO_2$ was emloyed in the formation of the carbonate complex and $^{12}C_2H_4$ was subsequently exposed to the carbonate covered silver surface at room temperature. The surface carbon produced from this reaction was then combusted by adsorbing additional oxygen, and both $^{13}CO_2$ and $^{12}CO_2$ were observed. Saturation exposure of $^{12}C_2H_4$ to a one-fourth monolayer of $^{13}CO_{3ads}$ yielded one-fourth monolayer of carbon-13 and three-fourths monolayer of carbon-12 which were subsequently combusted to carbon dioxide. The conclusion drawn from the above series of experiments is that the surface carbonate was active for the oxidative dehydrogenation of ethylene to surface carbon and water at room temperature

$$C_2H_4 + CO_{3ads} \rightarrow \rightarrow C_{ads} + H_2O. \quad (2)$$

This reaction did not occur when ethylene was adsorbed at low temperatures on a carbonate covered Ag(110) surface. Exposures of the carbonate covered Ag(110) surface to ethylene at 200 K resulted in the coadsorption of C_2H_4 as determined by UPS; however, heating of the sample caused only the desorption of C_2H_4 without destruction of the surface carbonate. The carbonate dissociated at higher temperatures to evolve CO_2 and O_2.

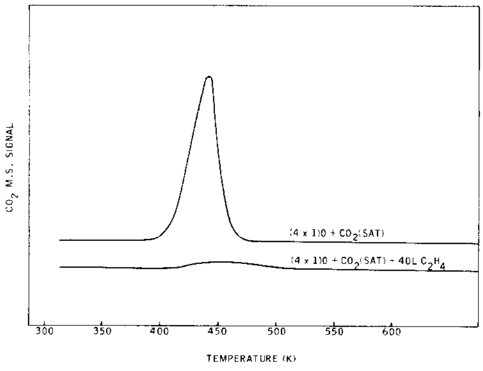

FIG. 5. CO_2 thermal desorption spectra from (4 × 1)O-covered Ag(110); (A) no C_2H_4 exposure; (B) C_2H_4 exposure prior to thermal desorption.

B. Chemistry of Surface Hydroxide

Exposure of several Langmuirs of water to the Ag(110) surface at 155 K resulted in the condensation of H_2O as determined by UPS and the corresponding HeI and HeII spectra are presented in Fig. 6. The agreement between the gas-phase H_2O ionization potentials (*15*) and the UPS peaks of H_2O adsorbed on silver demonstrate that water is molecularly adsorbed on this surface under these conditions. In addition the UPS spectra exhibit very low silver emission occurring at about −4.5 eV indicating that multilayers of H_2O formed on the Ag(110) surface at these low temperatures. Heating of the sample to 200 K resulted in the complete desorption of H_2O from this sur-

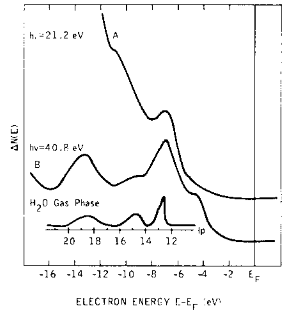

FIG. 6. $\Delta N(E)$ UPS of condensed H_2O on Ag(110) at 155 K; (A) $h\nu$ = 21.2 eV (B) $h\nu$ = 40.8 eV.

face, and the UPS spectrum of the clean Ag(110) was again obtained.

The adsorption of water on an oxygen atom covered Ag(110) surface led to the formation of a new surface intermediate. The silver surface was exposed to oxygen at room temperature to form a (2 × 1)O overlayer, cooled to 155 K, and then exposed to several Langmuirs of H_2O. UPS analysis revealed that multilayers of H_2O also formed over the oxygen-atom-covered silver surface. Upon heating the sample to 200 K the multilayers of H_2O desorbed and a new spectrum was formed that is shown in Fig. 7. This spectrum is essentially the same as the UPS spectrum of adsorbed hydroxide on Pt(111) which was also produced from the adsorption of water on an oxygen atom covered platinum surface (*16*). The positive identification of the surface hydroxide intermediate on platinum was achieved through the use of several different surface science techniques. The UPS peak at −8.2 eV was associated with the metal–oxygen bond and the peak at −11.0 eV was associated with the O–H bond of the surface hydroxide intermediate (*16*). The UPS OH characteristics observed in Fig. 7 began to disappear from the Ag(110) sample upon warming to 225 K, and completely disappeared at temperatures exceeding 245 K. The evolution of water from the Ag(110) sample in this temperature range was also observed in TPRS experiments. These experiments demonstrated that the adsorption of water on an oxygen atom covered silver surface yielded adsorbed hydroxide intermediates,

$$H_2O + O_{ads} \rightleftarrows 2OH_{ads} \qquad (3)$$

and the hydroxide intermediates reacted in the temperature range 225–245 K to form water that desorbed from the silver surface.

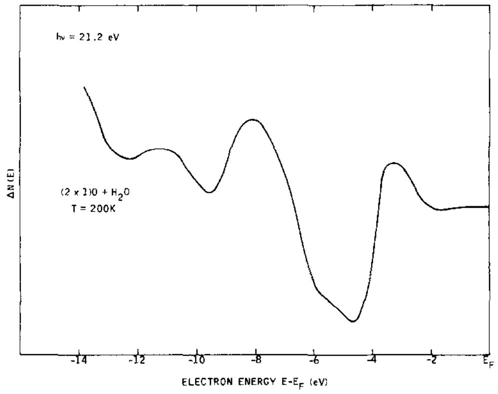

FIG. 7. $\Delta N(E)$ UPS of surface hydroxide on Ag(110) at 200 K.

The interaction between ethylene and adsorbed hydroxide intermediates on Ag(110) was examined at two different coverages of OH_{ads}. In one experiment the surface hydroxide was prepared from a (2 × 1)O overlayer, and in a second experiment the surface hydroxide was prepared from a (4 × 1)O overlayer. Exposure of 10 L of C_2H_4 to the hydroxide covered Ag(110) surfaces from 155 to 205 K produced no changes in the UPS features demonstrating that no adsorption or reaction of ethylene occurred on these surfaces. The UPS features of adsorbed ethylene were sufficiently different to detect its adsorption (*13*). Ethylene exposure to these surfaces at 250 K produced alterations in the UPS, but at these temperatures the surface hydroxides did not exist on the silver surface and ethylene was reacting with the adsorbed oxygen atoms (*13*). Under conditions where surface hydroxide is stable on the Ag(110) surface no reaction or coadsorption of ethylene was detected.

4. DISCUSSION

The present investigation demonstrated that carbon dioxide adsorbed on the oxygen atom covered Ag(110) surface to form a CO_3 complex, and saturation coverage was achieved when all of the adsorbed oxygen atoms were titrated by CO_2. The adsorbed carbonate decomposed to gaseous CO_2 and O_{ads} via first order kinetics during temperature programming experiments. The present adsorption/desorption behavior of carbon dioxide on oxygen covered silver is in excellent agreement with previous studies of this system (*2*, *4–7*). The excellent agreement between all of these investigators reveals that the carbonate intermediate is present on oxidized silver surfaces over a wide range of pressure, 10^{-8} to 10^2 Torr, and temperature, 150 to 500 K, and must be accounted for in kinetic models describing the oxidation of ethylene over silver (*1*).

The enhancement of oxygen atom recombination due to the presence of carbonate on silver claimed by Czanderna and Biegen (*5*) was not observed in the present study. Czanderna and Biegen concluded from their temperature desorption investigations that at high coverages of oxygen atoms on silver the presence of the coadsorbed CO_3 intermediate enhances the recombination and desorption of small quantities of oxygen atoms at the temperature of CO_2 desorption (*5*). They primarily arrived at this conclusion because of the tail observed in the carbon dioxide desorption curve. Although the maximum oxygen atom coverage examined in this study was somewhat lower, $\Theta = 0.25$, the desorption of O_2, beyond that expected from the formation of a small quantity of O_2^+/CO_2 in the ionizer of the mass spectrometer, was not observed to accompany the desorption of CO_2 from Ag(110). The tail observed in the CO_2 desorption curve by Czanderna and Biegen was most likely due to the readsorption of CO_2 on the oxidized silver surface because of their very slow heating rate (~2°C/min) and/or oxidation of a small quantity of surface carbon to CO_2 in this temperature range (*13*).

Information about the bonding of the surface carbonate intermediate on Ag(110) is obtained from comparison of the UPS features of CO_{3ads} in Fig. 3 with recent quantum mechanical calculations for CO_3^{2-} (*19*). The SCF-$X\alpha$ calculations for the CO_3^{2-} species of Tossell *et al.* are in general agreement with the earlier ab initio SCF-MO calculations of Connor *et al.* Both calculations predict the energy of the valence levels to lie in two groups split by approximately 6.0 eV and comprised of three levels in each group. The highest occupied levels are predominantly oxygen 2*p* nonbonding levels having a width of 1.9 or 1.4 eV. The second group, occurring at a lower energy, arises from carbon–oxygen bonding interactions; the two higher energy levels of this group are nearly degenerate and result from carbon 2*p* σ- and π-type interactions. These quantum mechanical calculations can be used to assign the principle UPS features for CO_3 adsorbed on Ag(110). The largest UPS peaks of CO_{3ads} occur in regions not complicated by appreciable overlap with the silver *d* emission, and appear near -3.3 and -8.5 eV. Additional smaller UPS features are also observed in Fig. 3, and of these the peak at -2.0 eV is the most distinct. In this context the UPS features near -3.3 eV are viewed to originate primarily from oxygen 2*p* nonbonding levels, and the features near -8.5 eV are considered to arise from carbon–oxygen bonding interactions. The comparison of the UPS features and the quantum mechanical calculations is specifically confined to the major observed emission features which are quite adequately accountable. UPS emission features due to silver–carbonate interactions are also observed, but their specific identification is complicated by the CO_3 emission features which currently precludes further analysis.

The adsorbed carbonate intermediate on Ag(110) was not completely inert under the present experimental conditions. The surface carbonate combusted ethylene at room temperature to yield adsorbed carbon and water. The mechanistic details of this reaction were not investigated, but this reaction probably proceeded via an oxidative dehydrogenation reaction analogous to the combustion of C_2H_4 by oxygen atoms on silver (*13*). At 200 K ethylene coadsorbed on the silver surface containing the CO_3 complex, but no reaction occurred between these adsorbates. The CO_{3ads} modified the adsorption of ethylene since ethylene does not readily adsorb on oxygen-free silver at 200 K. The interaction between CO_{3ads} and

C_2H_{4ads} could not have been very strong at these temperatures because ethylene desorbed without undergoing any reaction. The lack of reaction between CO_{3ads} and C_2H_{4ads} at 200 K reveals that the carbonate intermediate is less reactive than O_{ads} for ethylene combustion because the oxygen atoms react with ethylene at temperatures as low as 175 K (*13*). The new observation that ethylene can react with the carbonate adsorbed on silver has not been considered before, and previous investigators assumed that ethylene and CO_2 only compete for adsorption onto the oxygen atoms on the silver surface (*1*).

The inhibition of ethylene oxidation rate observed from the addition of carbon dioxide in the flow reactor studies is due to the formation of adsorbed carbonate on the oxidized silver surface. The present investigation demonstrated that the surface carbonate intermediate was less reactive than an adsorbed oxygen atom on silver towards ethylene oxidation; this property of CO_{3ads} suggests that the addition of CO_2 should lead to a decrease in the rate of ethylene oxidation as was observed in the flow reactor studies (*1*). The influence of the carbonate upon ethylene oxide selectivity could not be examined in the present study since under the conditions employed ethylene combustion was the only reaction pathway. At higher partial pressures of oxygen, as employed in the flow reactor studies, more than one type of active site is present on the oxidized silver surface (*18*) and CO_2 addition can affect the selectivity under these conditions by preferentially adsorbing on one of the sites to form a carbonate intermediate. The flow studies suggest that the nature of the promoters and supports have an effect on the active sites on the oxidized silver capable of adsorbing carbon dioxide.

Water adsorbed on the oxygen-free and oxygen-atom-covered Ag(110) surfaces as H_2O_{ads} and OH_{ads}, respectively. Although OH_{ads} desorbs as H_2O above 245 K it is present on an oxidized silver surface over a wide range of conditions as long as a partial pressure of water is maintained. The present investigation demonstrated that the surface hydroxide intermediate on silver was not reactive towards ethylene. This property of OH_{ads} suggests that the addition of H_2O should inhibit the rate of ethylene oxidation over silver as was observed in the flow reactor studies of Metcalf and Harriott (*1*). The influence of the surface hydroxide upon ethylene oxide selectivity could not be examined in the present study since under the conditions employed ethylene combustion was the only reaction pathway. The studies of Metcalf and Harriott demonstrated that addition of H_2O did not alter the selectivity of this reaction.

The competitive inhibition by CO_2 and H_2O during ethylene oxidation over silver catalysts was also examined by Metcalf and Harriott at a reaction temperature of 492 K (*1*). Although CO_2 and H_2O independently inhibited the rate of oxidation the addition of H_2O to a reactant stream containing CO_2 did not further decrease the reaction rate. This observation is consistent with the greater stability of CO_{3ads} (~445 K) than OH_{ads} (~225 K) on the silver surface, and consequently the carbonate dominated the inhibition process. It may further be possible that CO_2 enhanced the desorption of OH_{ads} from the silver surface but no evidence is presently available for such a surface process.

5. CONCLUSION

The adsorption of CO_2 and H_2O on oxygen atom covered Ag(110) was investigated with surface spectroscopic techniques. Carbon dioxide complexed with adsorbed oxygen atoms to form a surface carbonate intermediate, and the associative adsorption of water led to the formation of surface hydroxides. Ethylene did not react with CO_{3ads} and OH_{ads} below room temperature, but did exhibit reactivity toward CO_{3ads} at room temperature. These observations indicate that the formation of CO_{3ads} and OH_{ads} are responsible for the inhibiting effects of CO_2 and H_2O during ethylene oxidation over silver catalysts.

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