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Comparison of the Oxidation of Ethylene, Ethane, and Acetylene by Atomic Oxygen on Silver (110)

The oxidation of ethylene by atomic oxygen on silver (110) was recently studied with the modern tools of surface science in order to elucidate some of the fundamental surface reactions occurring during the oxidation of ethylene over silver (*1*). The following mechanism was found to take place during the combustion of ethylene by atomic oxygen on silver:

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

$$OH_{ads} + OH_{ads} \rightarrow H_2O + O_{ads}, \quad (2)$$

$$C_{ads} + 2O_{ads} \rightarrow CO_2. \quad (3)$$

Ethylene was oxidatively dehydrogenated by the adsorbed oxygen atoms to surface hydroxide and surface carbon atoms. The surface hydroxide intermediates rapidly reacted to yield water and adsorbed atomic oxygen, and the carbon atoms were subsequently oxidized by the oxygen atoms to carbon dioxide. The combustion of surface carbon, reaction step (3), only occurred at temperatures exceeding ~400 K, and at room temperature only reaction steps (1) and (2) occurred. Thus, at room temperature the oxygen atoms on the silver surface were selectively reacted to water by the hydrogen initially present in ethylene, and carbon was deposited on the surface according to the stoichiometry

$$C_2H_4 + 2O_{ads} \rightarrow 2C_{ads} + 2H_2O. \quad (4)$$

Auger analysis of the Ag (110) surface verified that only carbon was present after a saturation exposure of ethylene to the oxygen atom-covered silver. Temperature programming of the silver sample did not produce the desorption of CO_2, further demonstrating that oxygen was not coadsorbed on this surface. The amount of surface carbon formed on Ag (110) from ethylene was linearly dependent on the initial coverage of oxygen atoms. The total amount of carbon formed on the Ag (110) surface was determined by subsequently oxidizing the surface carbon to CO_2 in a series of temperature programmed experiments. In the present study the oxidation of acetylene and ethane by oxygen atoms adsorbed on silver (110) was also investigated since (1) the above mechanism for the combustion of ethylene by atomic oxygen suggests that these C_2 hydrocarbons should also follow the same reaction pathways and (2) small amounts of these hydrocarbons are present during ethylene oxidation over silver (*2–4*).

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). 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 ~10 K/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 (*5, 6*).

The Ag (110) sample was purchased from Materials Research Corporation and was

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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 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.

Oxygen (research grade) was introduced through a doser arrangement due to its low sticking probability on the clean silver surface (*7, 8*). The doser effectively supplied the front of the Ag (110) surface with an oxygen partial pressure that was considerably greater than the simultaneous oxygen background pressure. 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) (*7*). 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 at room temperature, only the *atomic* form of oxygen is present on the silver surface (*1, 7, 8*). Oxygen isotope experiments revealed that oxygen atoms were dissovled in the silver sample as well as adsorbed on the surface (*1*). The hydrocarbons exposure (research grade) were introduced via the background because of their high adsorption efficiency on the partially oxidized silver surface.

Acetylene and ethane did not adsorb at room temperature on an oxygen-free Ag (110) surface, but did react with atomic oxygen adsorbed on the Ag (110) surface to yield surface carbon at room temperature. The presence of surface carbon on the Ag (110) surface following saturation of an oxidized silver surface with C_2H_6 or C_2H_2 at room temperature was verified by TPRS and AES experiments. The combustion characteristics of the surface carbon, produced from the interactions of acetylene and ethane with the Ag (110)–(2 × 1) O surface, during TPRS experiments are presented in Figs. 1 and 2. In each of these runs a constant exposure of oxygen, 5 system Langmuirs, was given to the silver sample prior to the TPRS experiments. The combustion kinetics were complex because the amount of oxygen that actually adsorbed on the surface was dependent on the carbon surface coverage since carbon inhibited the adsorption of oxygen. Figures 1 and 2 show that many combustion cycles were required to completely burn off the carbon from the silver surface. The combustion characteristics of the surface carbon in the TPRS experiments reveal that the reaction order for this step was greater than unity because the peak maximum shifted to higher temperatures with decreasing carbon coverage (*9*). Similar results were previously obtained with ethylene. In these burn-off 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 produced from the interactions of ethane and acetylene with atomic oxygen on silver (110) at room temperature. Simultaneous AES analysis of the Ag (110) surface confirmed that carbon was initially present and was removed at the end of the combustion cycles (*10*).

The only difference observed between acetylene, ethylene, and ethane oxidation under the present conditions was the amount of surface carbon generated by each of these molecules. The amount of surface carbon generated by these C_2 hydrocarbons on a (2 × 1) oxygen atom-covered Ag (110) surface, as measured by the oxidation of surface carbon to CO_2, is

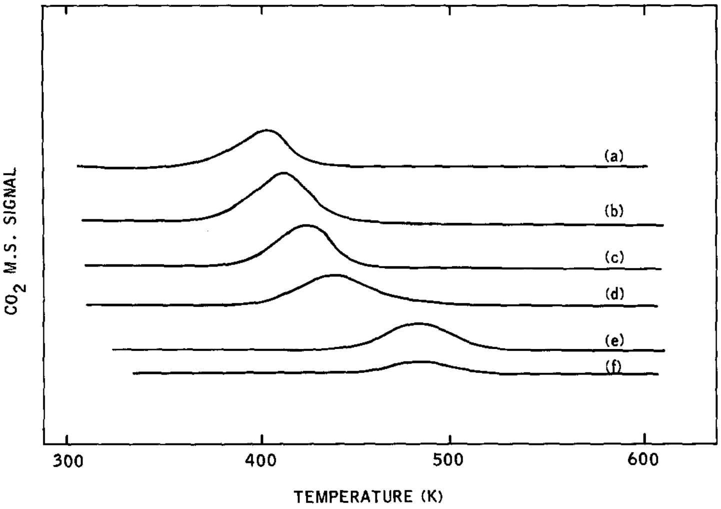

FIG. 1. Combustion of surface carbon, produced from the adsorption of ethane (saturation exposure) on a Ag (110)–(2 × 1) O surface, in a TPRS experiment (curve a initial burn-off; curve f final burn-off).

presented in Fig. 3. The quantity of surface carbon produced on the silver surface was directly proportional to the C/H ratio of the C_2 hydrocarbons. This observation is consistent with the following stoichiometries for the production of surface carbon from the oxidation of acetylene and ethane by atomic oxygen on Ag (110) at room temper-

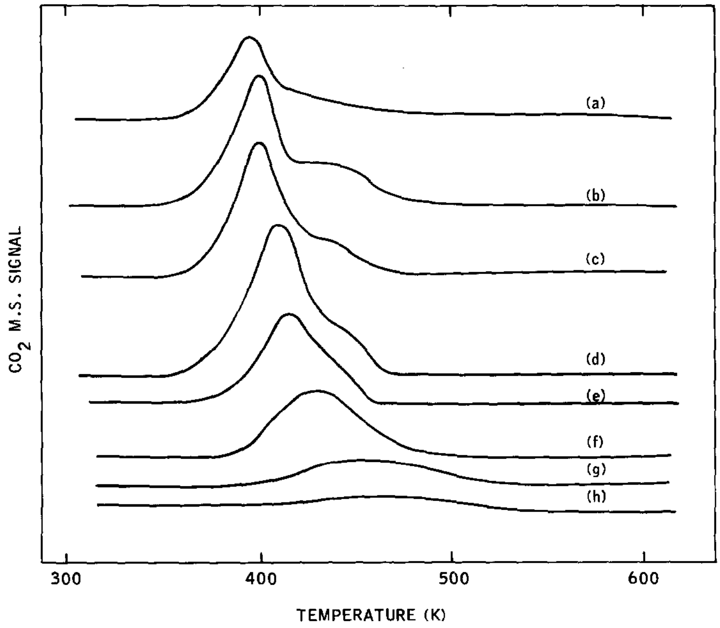

FIG. 2. Combustion of surface carbon, produced from the adsorption of acetylene (saturation exposure) on a Ag (110)–(2 × 1) O surface, in a TPRS experiment (curve a initial burn-off; curve f final burn-off).

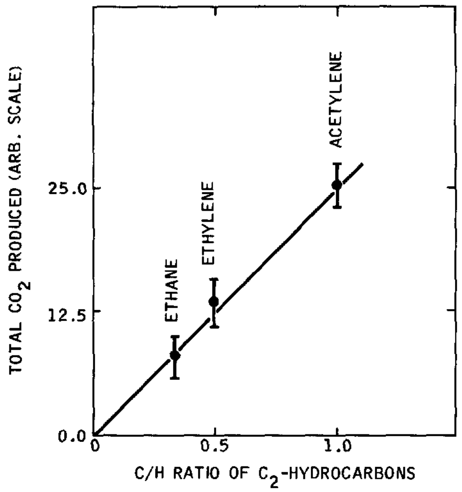

FIG. 3. Carbon deposition on Ag (110)-(2 × 1) O from various C_2 hydrocarbons at room temperature.

ature:

$$C_2H_2 + O_{ads} \rightarrow 2C_{ads} + H_2O, \quad (5)$$

$$C_2H_6 + 3O_{ads} \rightarrow 2C_{ads} + 3H_2O. \quad (6)$$

No attempt was made to rigorously determine the relative reactivities of the C_2 hydrocarbons toward the atomic oxygen adsorbed on the silver surface; since comparable hydrocarbon exposures were employed the reactivities were not dramatically different for the C_2 hydrocarbons.

These experiments revealed that the combustion of acetylene and ethane by atomic oxygen adsorbed on the Ag (110) surface followed the same reaction pathways as the combustion of ethylene by atomic oxygen on silver. The C_2 hydrocarbons were dehydrogenated by atomically adsorbed oxygen to surface carbon at room temperature, and the carbon was subsequently oxidized by atomic oxygen to carbon dioxide. The combustion of the C_2 hydrocarbons by atomic oxygen on silver can be represented by the following general mechanism:

$$C_2H_x + O_{ads} \xrightarrow{(x-1)O_{ads}} 2C_{ads} + xOH_{ads}, \quad (7)$$

$$OH_{ads} + OH_{ads} \rightarrow H_2O + O_{ads}, \quad (8)$$

$$C_{ads} + 2O_{ads} \rightarrow CO_2, \quad (9)$$

where $x = 2$, 4, or 6 for the different C_2 hydrocarbons. The only difference observed between acetylene, ethylene, and ethane oxidation under the present conditions was the amount of surface carbon generated by each of these molecules; the quantity of carbon produced for a (2 × 1) O coverage was directly proportional to the C/H ratio of the C_2 hydrocarbons. These experiments also demonstrated that oxygen atoms adsorbed on silver do not distinguish in their surface chemistry between hydrogen derived from acetylene, ethylene, or ethane molecules, and that the oxygen atoms are very effective in abstraction of hydrogen atoms from hydrocarbons.

The interaction of ethane with oxygen-covered and reduced silver powders was previously investigated by Czanderna with an ultramicrobalance *(11)*. Ethane was found to reversibly adsorb on the reduced silver surface at temperatures below 150°C, and to strongly chemisorb or form a dehydrogenated surface complex at higher temperatures. The reversible adsorption of ethane on the reduced silver at room temperature was dependent on the ethane partial pressure, and high partial pressures of ethane were employed (~10 Torr). In the present investigation low partial pressures of ethane were employed ($\sim 10^{-6}$ Torr), and ethane adsorption was not observed at room temperature on an oxygen-free Ag (110) surface. Czanderna further found that on an oxygen-covered silver surface ethane scavenged the surface of most of its oxygen, and left behind a residue that could be burned off in oxygen at elevated temperatures. These early experiments are in agreement with the present observations that ethane has a very weak interaction with an oxygen-free silver surface and readily reacts with oxygen adsorbed on silver, but Czanderna's experiments were somewhat complicated by the presence of ethylene in the ethane feed.

In conclusion, the C_2 hydrocarbons react with oxygen atoms on Ag (110) at room temperature to generate surface carbon, and the quantity of carbon is proportional to the C/H ratio for a given quantity of preadsorbed oxygen. The surface carbon is readily combusted to carbon dioxide by additional oxygen in subsequent TPRS experiments. The C_2 hydrocarbons follow the same reaction pathways in the presence of oxygen atoms on Ag (110) under the present experimental conditions.

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