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# The Surface Reaction of Carbon and Oxygen on a Stepped Pt(111) Surface

F. P. NETZER AND R. A. WILLE

*Institut für Physikalische Chemie, Universität Innsbruck, Innsbruck, Austria*

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The oxidation of surface carbon at elevated temperatures was investigated on a Pt(S)-[9(111) × (111)] surface using flash desorption mass spectrometry, LEED, and Auger spectroscopy. Randomly oriented graphitic carbon was deposited at the surface by thermal decomposition of ethylene. The reaction of carbon with adsorbed oxygen was followed by monitoring the respective desorption products in a mass spectrometer during heating cycles of the crystal. Three different reaction paths were detected differing in reaction product (CO vs $CO_2$) and oxidation temperature (700 vs 400°C). The amount and the structure of surface carbon as well as the temperature determine the prevailing reaction mechanism at a given stage of the oxidation. The various adsorbed surface species were probed by high resolution Auger spectroscopy during the course of the oxidation. The results are discussed in terms of different surface complexes and of a different chemical environment of adsorbed oxygen as being responsible for the various reaction mechanisms.

## INTRODUCTION

The build-up of carbon overlayers on metal surfaces by segregation from the bulk phase or by decomposition of carbon-containing adsorbed molecules is a well-known phenomenon and of equal annoyance to both surface physicists and chemists. In order to remove the unwelcome carbon from the surface rather rigorous cleaning procedures have to be adopted. Since it has been recognized that merely heating in a vacuum is insufficient to deplete transition metal surfaces from carbon, the oxidation of carbon with oxygen at elevated temperatures is currently being used as a cleaning procedure. Although this reaction is used in most surface science laboratories little attention has been paid so far to the mechanism of this reaction and to the role of the underlying metal surface. In this paper we report results of an investigation of the oxidation of surface carbon on a stepped platinum (111) surface. As carbonaceous overlayers play an important role in hydrocarbon catalysis on platinum surfaces (*1*), the oxidation reaction was studied on a stepped rather than a flat platinum surface, thereby approaching conditions nearer to those encountered in practical catalysis. Due to the experimental conditions outlined in the next section, we confined our investigation to the reaction between surface carbon and adsorbed oxygen using LEED, thermal desorption mass spectrometry, and Auger spectroscopy. The use of high resolution Auger spectroscopy as a "fingerprinting" technique for surface reaction studies is demonstrated. The results will be discussed by comparison with oxygen and CO adsorption data from the same surface, which form a part of a wider investigation



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program of chemisorption characteristics on stepped platinum surfaces (*2*).

## EXPERIMENTAL PROCEDURE

Experiments were carried out in a stainless-steel UHV system fitted with a three-grid LEED optics, a quadrupole mass spectrometer, and the usual facilities for crystal manipulation and cleaning. Typical base pressure was $<5 \times 10^{-11}$ Torr. Gases were introduced from an ion-pumped stainless-steel gas inlet system by means of a capillary which allowed a relatively high pressure at the crystal surface without a simultaneous pressure rise in the total system. High resolution Auger spectra were recorded with a Leybold–Heraeus concentric hemispherical analyzer operated in the lock-in mode to yield spectra in $dN/dE$ form. The geometrical arrangement between analyzer, sample, and electron gun is shown in Fig. 1. Due to the large crystal–analyzer distance ($\sim$70 mm), the acceptance solid angle of the analyzer is rather narrow (15°). The resulting Auger spectra are therefore partly influenced by angular effects of the Auger emission process and sometimes deviations from literature data relative intensities of various Auger peaks are observed. In this study the surface normal of the crystal was kept in the direction of the analyzer axis. The spectrometer was run at a resolution of $E/\Delta E \approx 400$, which was sufficient for the present investigations.

The crystal was prepared and cleaned according to standard procedures (*3*). Both sides of the elliptically shaped crystal disk exposed the same high-Miller-index stepped surface (997) which may be denoted in surface nomenclature as Pt(S)-[9 (111) $\times$ (111)] (*4*). The clean surface showed a sharp (1 $\times$ 1) LEED pattern with doublets characteristic of the stepped surface (see Fig. 5a). Carbon was deposited onto this surface by thermal

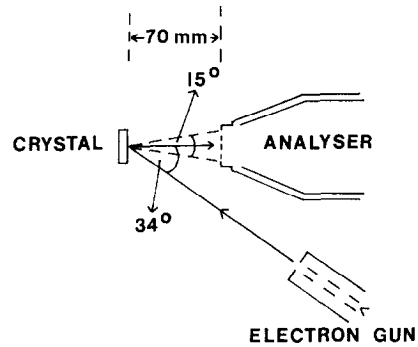


FIG. 1. Analyzer geometry in the plane defined by the electron beam and the analyzer axis.

decomposition of gas-phase ethylene at 650°C at typical exposures of 3000 $L$ (1 $L$ = 1 $\times$ $10^{-6}$ Torr·sec). This resulted in a graphitic carbon overlayer randomly oriented with respect to the substrate as indicated by the ring-like LEED pattern and the shape of the C Auger signal. The thickness of the carbon deposit is estimated to be between one and five monolayers as suggested by the persistence of substrate LEED spots. As reported by Lang (*5*), the amount of carbon deposition according to the above-mentioned procedure is limited and not uniformly distributed over the surface. We also obtained evidence for a patchy carbon overlayer which we will discuss below. However, no preferential orientations of the various carbon domains were observed in this work, nor could any ordered overlayer be detected.

The oxidation reaction was studied in the following way: The graphitized surface was exposed to oxygen (typically 3000 $L$) at room temperature. The influence of the oxygen exposure on the reaction was studied separately and found not to be crucial as long as saturation adsorption conditions were warranted. After pumpdown to $<5 \times 10^{-10}$ Torr, the surface was heated at linear heating rates between 5 and 50°C/sec, and the desorbing particles were detected in the mass spectrometer. We will refer to this procedure as an *oxidation step*. Many oxidation steps

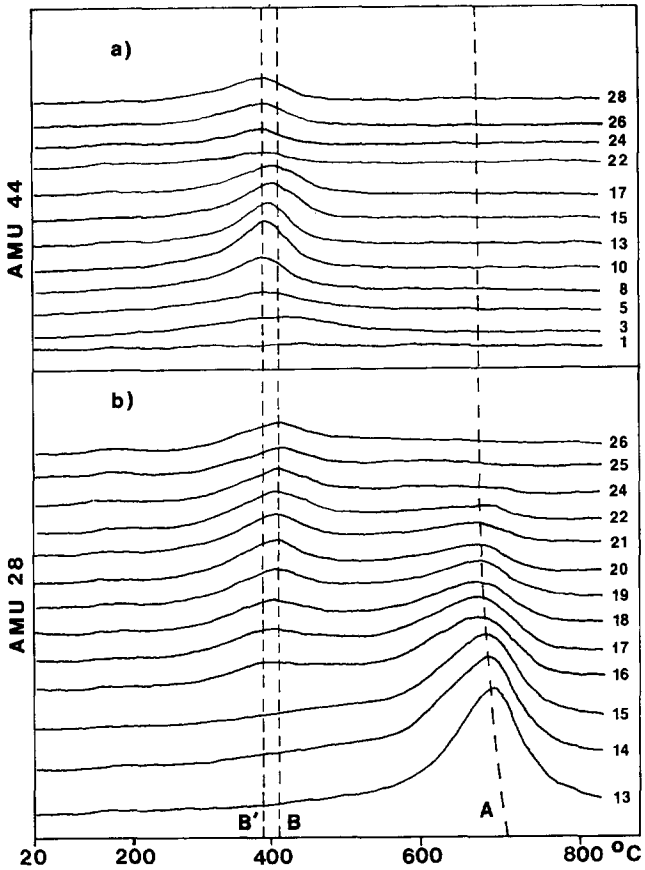


FIG. 2. $CO_2$ (a) and CO (b) desorption traces during a series of consecutive oxidation steps. Heating rate, 50°C/sec.

were repeated until the entire carbon layer was oxidized and the clean surface was regenerated. It is evident that due to the present experimental conditions our study is confined to the reaction between surface carbon and adsorbed oxygen, as the reaction between surface carbon and oxygen in the gas phase can be neglected during exposure at room temperature. However, we will show that with this experimental set-up the role of different surface complexes and of the underlying Pt surface can be investigated.

## RESULTS AND DISCUSSION

After exposing the C-covered Pt surface to oxygen at room temperature, three desorption products were detected in the mass spectrometer during heating cycles of the crystal: $CO_2$, CO, and $O_2$. It is obvious that the two former desorption products are the result of the reaction under investigation, whereas the desorbing oxygen can originate either from carbon or Pt sites. The absolute and relative amounts of the three desorption products were strongly dependent on the number of preceding oxidation steps and on the amount of carbon present at the surface. Figure 2 shows typical desorption spectra of $CO_2$ (a) and CO (b) according to sequences of oxidation steps. The numbers indicated in the figure refer to consecutive oxidation steps. $CO_2$ desorbs in a broad peak around 400°C (Fig. 2a) which is slowly built up from oxidation step to

oxidation step until it reaches a maximum after 10–15 oxidation steps. After a decrease, the desorbed $CO_2$ amount remains roughly constant after 20 oxidation steps (compare Fig. 3). Toward the end of the surface oxidation, the decreasing carbon concentration becomes the dominant factor and the amount of all reaction products decreases simultaneously. The position of the $CO_2$ peak, denoted as B′, is essentially constant in temperature.

Two CO desorption peaks can be recognized in Fig. 2b which show pronounced relative intensity variations as a function of consecutive oxidation steps. At first, peak A grows slowly (not shown in the figure) up to a maximum between oxidation steps 10–15, after which a steady decrease is observed. We note also a shift of the peak maximum from 710 to 675°C with an increasing number of oxidation steps. Peak B, at a slightly higher temperature than the $CO_2$ peak, B′, appears first between oxidation steps 13–15, shows a maximum around oxidation step 22, and then decreases as the amount of surface carbon decreases. The maximum of B shows no temperature shift as oxidation goes on.

The trends discussed above, i.e., the quantitative variations of the various oxidation products during the course of the oxidation, are depicted in Fig. 3. It should be noted that the three curves are not scaled properly due to the fact that different mass spectrometer sensitivity settings were necessary in order to record the different reaction products, CO and $CO_2$. The peak areas under the desorption curves, taken as a measure of the desorbing amount, are therefore given in arbitrary units. The experimental data of curve A show strong fluctuations which are possibly due to difficulties in the graphical integration procedure of broad, overlapping peaks. Therefore, no quantitative information can be derived from Fig. 3. However,

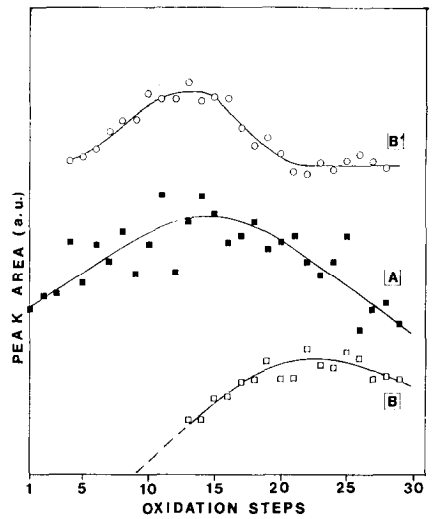


FIG. 3. Desorption peak areas of various reaction products during the course of the oxidation. A, CO at 700°C; B, CO at 400°C; B′, $CO_2$ at 400°C.

the course of the different desorption peaks reveals some interesting aspects. Peak A (CO) and peak B′ ($CO_2$) exhibit a rather similar behavior, whereas peak B (CO) shows a very different course as oxidation proceeds. This suggests that three different oxidation mechanisms, depending on the stage of the oxidation, take place and have to be accounted for in an interpretation of the oxidation process.

Desorption spectra of oxygen from the C-covered Pt surface are compared with those from the clean Pt surface in Fig. 4. Figure 4b shows $O_2$ desorption traces during various oxidation steps, Fig. 4a the $O_2$ desorption from the clean surface as a function of exposure. We note that (i) the amount of oxygen desorbing from the C-covered surface increases as the oxidation proceeds, (ii) the shapes of the desorption curves in Fig. 4b remain essentially unchanged, and (iii) the desorption curves of Fig. 4b exhibit shapes very similar to the ones obtained at saturation from the clean surface. These results indicate that the oxygen desorbing during oxidation steps originates from Pt sites and is a measure of the carbon-free portion of the surface.

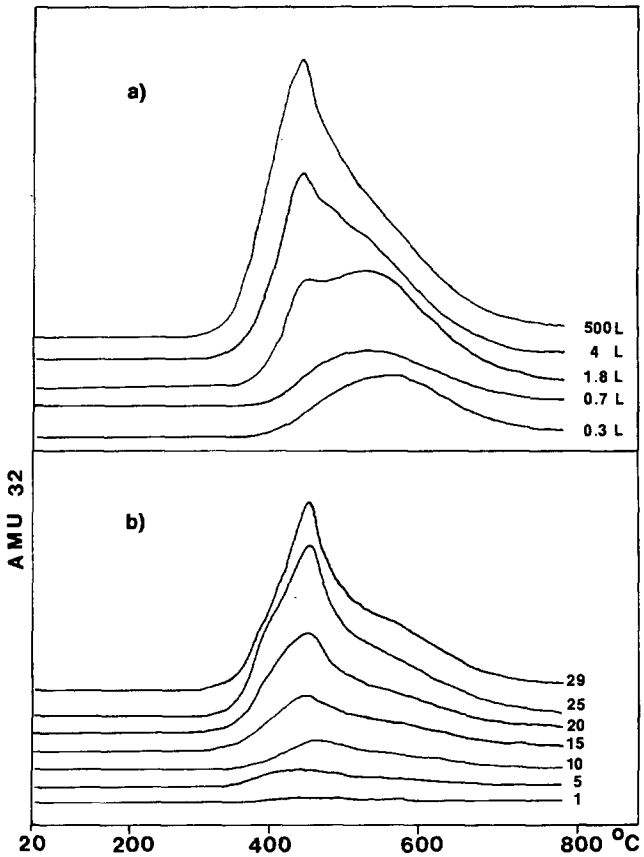


FIG. 4. Oxygen desorption spectra. (a) Desorption from the clean surface. (b) Desorption during oxidation steps. Heating rate 50°C/sec.

These carbon-free areas are saturated with oxygen during oxidation steps, and the oxygen chemisorptive bond is almost not influenced by the adjacent patches of graphitic carbon. Furthermore, even on the surface saturated with carbon, i.e., during the initial stages of the oxidation, there are small areas consisting of undisturbed "clean" Pt sites.

This view of a patchy carbon overlayer is further supported by LEED evidence. After about 16–18 oxidation steps an oxygen–(2 × 2) LEED pattern superimposed on the characteristic ring-like pattern of graphitic carbon was observed (Fig. 5b). After a suitable number of oxidation steps, the areas of the "clean" Pt domains are large enough to accommodate an ordered oxygen overlayer observable by LEED. It seems that the oxidation of the patchy carbon overlayer proceeds fastest at the boundaries between carbon and platinum thereby reducing the size of the carbon islands. The (2 × 2)–O structure appears when the B peak of CO is just clearly discernible.

Carbon and oxygen Auger line shapes of $O_2$ and CO chemisorbed on the clean Pt surface and of the surface species present during various oxidation steps are compared in Fig. 6. Two sets of spectra were taken during the oxidation steps: (a) after $O_2$ saturation at room temperature and (b) after flashing the crystal to 530°C which only leaves the surface species responsible for the high-temperature CO desorption peak (A) present at the surface.

The O KLL peak shapes of $O_2$ and CO

adsorbed on the clean Pt surface (two top spectra of Fig. 6) are in excellent agreement with those published recently by Grant and Hooker (*6*). The C KLL peak shape of CO is somewhat different from that reported in (*6*), especially with regard to the sharp doublet characteristic for molecularly adsorbed CO which is only indicated in Fig. 6. Very recent investigations (*2*) have shown, however, that this is partly due to the effect of the modulation voltage of 5 Vpp, where the doublet is only poorly resolved in our spectrometer, and partly to the effect of the electron beam (the C KLL spectra being run after the O KLL) (*2*, *7*).

The O KLL spectra recorded during oxidation steps at room temperature [denoted as (a) in Fig. 6] seem to be superimposed "$O_2$-like" and "CO-like" spectra at the earlier stages of the oxidation (up to oxidation steps 12–14), whereas with progressing oxidation the "$O_2$-like" character clearly dominates. The spectra taken after flashes to 530°C [(b) in Fig. 6] are generally "CO-like" although some differences from CO have to be noted. The initial C KLL spectra show the expected shape of graphitic carbon because of large excess carbon on the surface and tend to become more "CO-like" after extensive oxidation. It seems therefore that at room temperature surface species involving O–Pt bonds and surface species involving O–C bonds are present at the surface, whereas after flashes to 530°C the O–C bond containing species are predominant. From the shapes of the O KLL spectra and their variations during the course of the oxidation, we conclude that the surface complexes giving rise to the desorption peak A of CO and possibly also to the B′ peak of $CO_2$ have oxygen bound to carbon at the surface, whereas there are no indications that oxygen must be prebound to carbon for the B peak of CO to appear (see the "$O_2$-like" spectra after extensive oxidation where the B CO is the prevailing reaction product).

What are the likely implications to be drawn from these experimental results? There are three ways surface carbon can be oxidized by surface oxygen depending on the dimensions and the structure of the carbon overlayer and on the temperature. We believe that the surface complexes yielding $CO_2$ at 400°C and CO at 700°C involve oxygen bound to carbon at the surface. The Auger results and the similar behavior of the A peak and the B′ peak

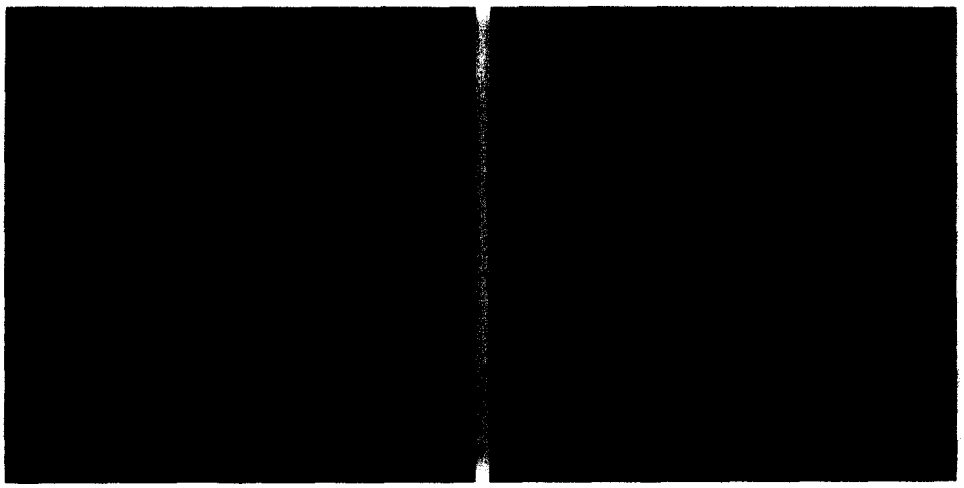

FIG. 5. (a) LEED pattern of the clean Pt(S)-[9(111) × (111)] surface. $E$ = 90 eV. (b) (2 × 2)-O LEED pattern superimposed on the ring-like graphitic C pattern. $E$ = 75 eV.

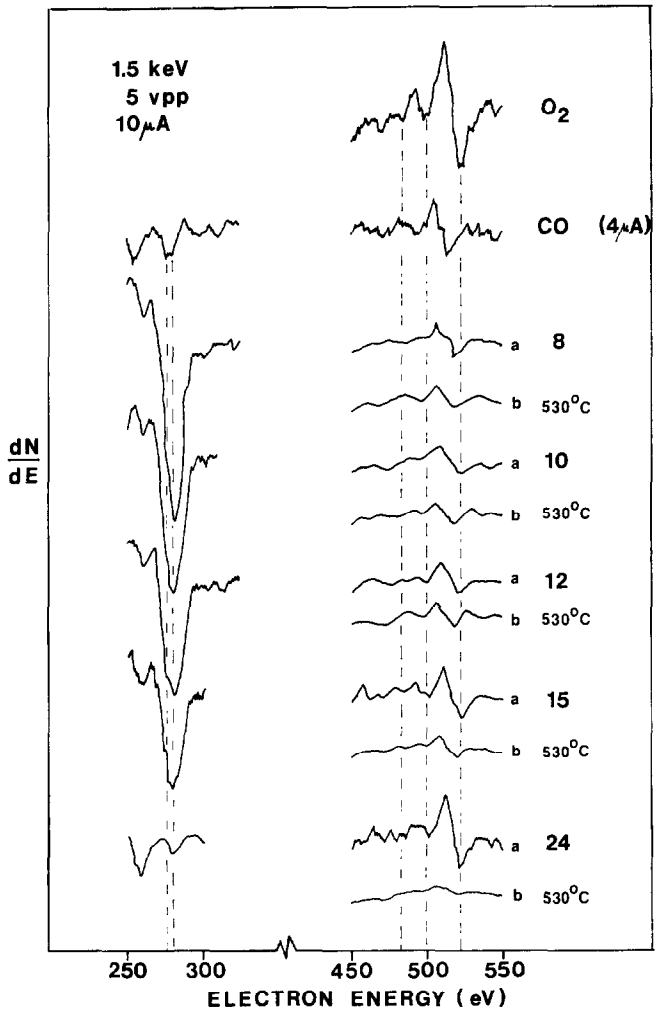


FIG. 6. C KLL and O KLL Auger spectra of $O_2$ and CO adsorbed on clean Pt and of the surface species present during oxidation steps. Numbers refer to consecutive oxidation steps (for details, see text).

during the course of the oxidation support this assumption. These surface complexes differ distinctly from molecularly adsorbed CO on the same stepped Pt surface which is desorbed below 330°C (*2*), although some similarities in the oxygen bonding may be implied from the Auger results. Similar types of surface complexes have been postulated for the adsorption of oxygen on various carbon surfaces (*8*). According to those investigations a $CO_2$-type complex decomposes at 400°C yielding gaseous $CO_2$, whereas desorption of CO from a CO-type surface complex sets in above 600°C. Although done under completely different conditions, these results closely parallel the findings of this study. A considerable number of free Pt sites is necessary for the B CO peak at 400°C to appear in the desorption spectra. We therefore propose that the B CO is formed at an elevated temperature (~400°C) by reaction between oxygen adsorbed on Pt sites and carbon at the boundaries of the patchy carbon overlayer.

The oxidation rate is very slow at the initial stages of the oxidation. This indicates that the adsorption of oxygen on

graphitic carbon at room temperature is slight under UHV conditions. Support for this is found by Auger spectroscopy where the oxygen signal was detected first after several oxidation steps. As it may be assumed that oxidation proceeds fastest at the steps and kinks of the Pt–C boundary [see also (*8*)], the increase of the oxidation rate with the progress of oxidation may be understood in terms of structural changes of the boundary lines. These changes might also be responsible for the shift of the A peak with an increasing number of oxidation steps.

The catalytic role of the Pt surface seems to consist mainly in its ability to yield oxygen atoms at the surface thereby facilitating the formation of carbon–oxygen surface complexes (A, B′) or enabling direct reaction at elevated temperatures (B). The initial induction period of the oxidation reaction, when the bare Pt surface is constricted to very small areas, underlines this important property of the Pt surface.

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