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Characterization of carbonaceous overlayers on platinum by catalytic oxidation

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Carbonaceous overlayers formed from ethylene on polycrystalline Pt have been characterized with AES and SIMS. The reactivity of these deposits towards oxygen depends sensitively on their nature. Hydrogen-rich hydrocarbon deposits on Pt oxidize at 410–420 K, carbidic C and CH species in the range 450–470 K, and graphitic carbon at 565–570 K. The results confirm that oxidation is a suitable test for the reactivity of catalytically relevant carbonaceous overlayers on Pt.

1. Introduction

Every metal which catalyzes a reaction of hydrocarbons is during the reaction covered by an overlayer. This adsorbate layer consists of carbon and hydrogen, and determines together with the metal the properties of the catalytic system. Four distinct types of carbonaceous deposits can be identified, which differ in reactivity, hydrogen content, and extent of graphitization. We will use the following nomenclature. Deposits consisting of adsorbed hydrocarbons are called molecular, single C atoms or CH species carbidic, and unreactive, polycyclic aromatic carbons graphitic. A less polymerized and more hydrogen-rich precursor to graphitic carbon is called amorphous carbon.

Previous work in our laboratory has revealed that AES and negative SIMS form a powerful combination to characterize carbonaceous overlayers on noble metals and alloys. The oxidation of carbonaceous deposits is of practical interest, because catalysts deactivated by excessive carbon deposition are regenerated by burning-off the carbon. Oxidation may also provide a convenient test for the reactivity of carbon deposits. Model studies of the reaction of oxygen with carbon layers on Ni and Fe have been reported. However, we are not aware of model studies on the oxidation of carbonaceous layers on platinum.

In this paper we show that the oxidation of three different types of carbonaceous layers on polycrystalline Pt occurs in well separated temperature regions. The results confirm that oxidation is a suitable reaction to test the reactivity of carbon overlayers on Pt.

2. Experimental

Experiments were carried out in an XPS/AES/SIMS spectrometer (Perkin–Elmer, PHI 550) equipped with a reaction chamber. Auger spectra were measured differentially with a defocused 4.5 μA beam of 2 keV electrons and a spot diameter of 0.5 mm, the modulation amplitude used was 2 eV. SIMS spectra were measured with a 50 nA beam of 1 keV Ar ions, which was rastered over the sample.

A high purity Pt foil (Highways), spotwelded on tantalum wires, was cleaned by several cycles of 5 keV Ar sputtering and annealing at 1000 K. A subsequent Auger analysis showed no contaminants within the range of accuracy. Carbon was deposited on Pt from 67 Pa (0.5 torr) C/H (Messer Griesheim). Oxidation was carried out in 67 Pa of 0.5% O2-in-He. After reaction the sample was cooled to 300 K, and transferred into the uhv chamber after evacuation of the reaction chamber.

3. Results

3.1. Carbonaceous deposits on Pt. Carbonaceous deposits of different nature were made by treating Pt with C/H at 325, 525 and 775 K, and investigated with AES and SIMS. Carbon coverages were calculated from the intensity ratio of the C and Pt Auger peaks at 272 and 228 eV, respectively, and are given in Table 1. In the calculations the empirical relations of Biberian and Somorjai were used. SIMS patterns of the carbonaceous deposits are shown in Figure 1. As discussed elsewhere, the negative ions, C/H and C/H+, display the best sensitivity for the state of the carbonaceous deposits. The C/H+ intensities in Figure 1 indicate that deposits formed at 325 K are rich in hydrogen (relatively high intensities of C/H and C/H+), and that carbon formed at 775 K is depleted in hydrogen (high C intensity). We express the information on the hydrogen content in one number by defining a parameter h as the ratio \((C_2H+ + C_2H_2)/(C_2 + C_2H+ + C_2H_2)\), where the ions represent the intensities of their corresponding peaks in the SIMS spectra. With the spectrometer used, and the beam conditions specified, the values of h fall in the range between close to zero (0.03 for graphite on Pt annealed in uhv at 800 K) and about 0.7 for ethylene adsorbed on Ir at 300 K, where ethylidyne (=CCH3) is expected to form. The extent of polymerization of the carbonaceous deposit is reflected in the
with respect to the oxidation of molecular carbon on Pt, it is important to note that it makes a difference whether \( \text{C}_2\text{H}_4 \) is decomposed first and then exposed to oxygen, or the other way round.

**3.2. Oxidation of carbonaceous deposits on Pt**

Auger spectra of the graphite deposit, formed from \( \text{C}_2\text{H}_4 \) at 775 K, after various treatments in 67 Pa of 0.5% O\(_2\)-in-He are shown in Figure 2. The top spectrum, carbon exposed to O\(_2\) at 550 K, is still identical to that of the initial carbonaceous deposit; its shape is characteristic for graphitic or amorphous carbon\(^{12}\). The carbon coverage is about 2 monolayers (ML). After oxidation at 560 K a considerable fraction of the carbon has been removed; the amount of the remaining carbon corresponds roughly to 0.9 ML. Note that the carbon peak exhibits a shoulder around 265 eV (see arrow), which was absent in the spectrum of the original deposit. This fine structure is characteristic of either carbidic or molecular carbon\(^{13}\). After reaction at 567 K almost all carbon has been removed by oxygen, only about 0.1 ML of carbon is left, which decreases to half that value after reaction at 575 K. A lower C coverage could not be obtained by reaction with oxygen in the reactor. Hence, we conclude that graphitic carbon on Pt can be removed by oxygen at temperatures in the range form slightly below 560–567 K.

Figure 3(a) shows the oxidation of a carbonaceous deposit formed from \( \text{C}_2\text{H}_4 \) at 525 K. The top spectrum corresponds to the clean Pt foil, the second to that of the carbon overlay formed at 525 K. The coverage of the latter is 1.2 ML. As molecular and carbidic carbon are more sensitive to degradation by electron irradiation than graphitic carbon, the width of the energy channels was increased and the measuring time per channel shortened, in order to decrease the time of exposure to the primary electron beam. Consequently, the spectra of Figure 3 are less detailed and contain more noise than those of Figure 2. Nevertheless, the spectra of Figure 3(a) clearly show that the oxidation of the carbonaceous deposit formed from \( \text{C}_2\text{H}_4 \) at 525 K starts around 450 K and is completed at 470 K.

Finally, the oxidation of the molecular carbon on Pt, formed from \( \text{C}_2\text{H}_4 \) at 325 K, takes place between 410 and 420 K (Figure 3(b)). Here a new carbonaceous deposit was prepared after each Auger analysis because electron beam induced degradation of the molecular deposit could be observed after recording more than two Auger spectra. For example, a molecular deposit which had been exposed to the electron beam during the time needed for four spectra, was oxidized at 470 K, whereas the oxidation temperature of a freshly prepared deposit was between 410 and 420 K. Note, that this electron beam induced degradation was not observed for carbonaceous layers deposited at 525 K.

### 4. Discussion

The most important conclusion from the present results as collected in Table 1, is that different carbonaceous deposits on Pt oxidize at different temperatures. This means that oxidation is indeed a suitable test reaction for the reactivity of carbon in carbonaceous overlayers on metals. The characteristic oxidation temperatures are sufficiently well separated to make temperature programmed oxidation (TPO) of carbonaceous deposits feasible.

The oxidation temperature of graphitic carbon on Pt, 565 K, is in good agreement with results on coked Pt/Al\(_2\)O\(_3\) catalysts reported by Barbier et al\(^{16}\). The TPO profile of a deactivated Pt/Al\(_2\)O\(_3\) catalyst shows a peak at 575 K, attributed to the oxidation of coke on the metal, and a peak at 725 K, attributed to coke on the Al\(_2\)O\(_3\) support. The gasification of coke on catalysts which are inactive for oxidation reaction requires a temperature of about 775 K\(^{5}\). The fact that all carbonaceous deposits on Pt studied here can be oxidized at considerably lower temperatures confirms that the oxidation is catalyzed by Pt.

With respect to the oxidation of molecular carbon on Pt, it is important to note that it makes a difference whether \( \text{C}_2\text{H}_4 \) is decomposed first and then exposed to oxygen, or the other way around.
around as in refs 13, 17, because ethylene interacts differently with oxygen-precovered Pt(111) than with clean Pt(111). When the system O/Pt(111) is exposed to C\textsubscript{2}H\textsubscript{4}, CO\textsubscript{2} evolution is already observed between 300 and 400 K\textsuperscript{13,17}. In our experiments, the molecular carbonaceous deposit, presumably ethylidyne, oxidizes at 415±5 K, as the spectra in Figure 3(a) show.

The fine structure in the Auger spectra observed during the oxidation of graphitic carbon (see arrow in Figure 2) is typical for carbidic carbon atoms, adsorbed hydrocarbon fragments or adsorbed CO\textsuperscript{5}. Its presence indicates that a fraction of the graphitic carbon has been converted by oxygen without having left the surface. Considering that CO\textsubscript{2} and CO desorb at temperatures well below 560 K, it seems likely that the Auger fine structure at 265 eV is due to carbon from destroyed aromatic rings. SIMS spectra were of little use in studying the oxidation of carbonaceous deposits on Pt. For example, one of the effects of exposing graphitic carbon on Pt to O\textsubscript{2} at room temperature was that the emission of C\textsubscript{2}H\textsuperscript{-} and C\textsubscript{2}H\textsubscript{2}\textsuperscript{-} increased with respect to that of C\textsubscript{2}, implying that the \( h \) parameter loses its meaning for carbon deposits under O\textsubscript{2}. The low intensities of Pt\textsuperscript{+}, PtC\textsubscript{10}H\textsubscript{16}\textsuperscript{+} and PtCO\textsuperscript{+} ions in positive SIMS make a potentially interesting study of the oxidation mechanism with positive SIMS impossible, at least with our spectrometer. For the future we intend to study the oxidation of carbonaceous deposits on Rh and Ni, where the desired secondary ions do have sufficient intensity.

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References