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The adsorption of CCl_4 on Ag(1 1 1): Carbene and C=C bond formation

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Abstract

The adsorption of CCl_4 on Ag(1 1 1) has been investigated from 100 K to 300 K using absolute sticking probability measurement, temperature programmed desorption, Auger electron spectroscopy, low energy electron diffraction, ultra-violet photoelectron spectroscopy and X-ray photoelectron spectroscopy. At 100 K, CCl_4 adsorbs molecularly with a sticking probability of 1.0, forming a (3×3) adsorption structure. At 300 K the following overall reaction occurs,

$$2CCl_{4(g)} \rightarrow 4Cl_{(chem)} + C_2Cl_{4(g)},$$

with an initial sticking probability of $S_0 = 0.25$, indicating that activated dissociative adsorption is the initial step in the above reaction. The saturated surface at 300 K consists entirely of chemisorbed chlorine which undergoes an order/disorder transition to a sharp $(\sqrt{3} \times \sqrt{3})R30°$ structure on cooling below 180 K. Temperature programmed desorption of CCl_4 adsorbed at 100 K shows a multilayer peak at 140 K and a first layer peak at 203 K, where part of the molecularly adsorbed CCl_4 desorbs and the rest is converted to a surface carbene, $:CCl_2$, and chemisorbed chlorine. At 248 K the adsorbed carbenes react to form C_2Cl_4 which promptly desorbs, as it is formed above its normal desorption temperature of 210 K.

Keywords: Low energy electron diffraction (LEED); Photoelectron spectroscopy; Thermal desorption spectroscopy; Sticking; Surface chemical reaction; Chlorine; Silver; Alkenes

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1. Introduction

The adsorption of carbon tetrachloride has been studied on several single crystal substrates, as reviewed by Chesters and Lennon [1], but only Polanyi and co-workers have studied the adsorption of CCl_4 on Ag(1 1 1) [2–4]. Using temperature programmed desorption (TPD) and Auger electron spectroscopy (AES), they reported that CCl_4 adsorbs dissociatively at room temperature to form chemisorbed chlorine with a coverage of ~0.5 ML (1 ML is a concentration equal to the substrate surface atom concentration). For adsorption at ~110 K, they reported molecular adsorption such that when TPD was carried out on the multilayered adsorbate, molecular desorption of CCl_4 occurred over a broad temperature range, finishing with a desorption peak at 210 K. They further reported the evolution of tetrachloroethene, C_2Cl_4, from the surface at ~270 K and formation of chemisorbed chlorine on the surface.

In this work we study the reaction of CCl_4 on Ag(1 1 1) between 100 K and 300 K using low energy electron diffraction (LEED), AES, He I ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), and line of sight mass spectroscopy (LOSMS) to measure TPD and absolute sticking probabilities (S). We find that reaction at room temperature occurs with an initial sticking

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probability (S_0) of 0.25, to give a chemisorbed chlorine adlayer with a $(\sqrt{3} \times \sqrt{3})R30°$ structure having a coverage of 0.33 ML with no carbon deposition; the overall reaction with the silver surface is

$$2CCl_{4(g)} \rightarrow C_2Cl_{4(g)} + 4Cl_{(chem)}. \tag{1}$$

For adsorption at 100 K, we find molecular adsorption occurs with a sticking probability of $S = 1.0 \pm 0.01$. LEED studies of this monolayer at 100 K showed a (3×3) pattern, which can be explained using the idea proposed in [2] that CCl_4 will most likely sit with three of the chlorine atoms in contact with the surface. TPD of the molecularly adsorbed CCl_4 is in broad agreement with previous work [2], including evolution of C_2Cl_4, except that our temperatures are slightly lower. Using UPS and XPS, we identify the carbene, $:CCl_2$, as the stable surface species which forms the C_2Cl_4 product at $T \approx 250$ K.

While the adsorption, and reaction, of CCl_4 with Ag(1 1 1) is of interest in itself, it is also of interest as a convenient way of depositing chemisorbed chlorine cleanly onto the surface. This may be of use in studies of the role of chlorine in the catalytic epoxidation of ethene, where a method of dosing the surface with chlorine without recourse to using elemental Cl_2 may be advantageous.

2. Experimental details

Experiments were carried out in a UHV chamber, which has already been described [5]. LOSMS were taken using a VG SX300 quadrupole mass spectrometer, modified to operate in pulse counting mode, shrouded by a liquid nitrogen cooled cryopump such that only molecules travelling by line of sight from a patch ∼9 mm in diameter on the surface could reach the ionisation region of the mass spectrometer [6–8]. For TPD, the sample temperature was ramped at $0.5\ \mathrm{K\ s^{-1}}$ while monitoring the desorbing species using LOSMS. Absolute sticking probabilities, S, were measured by monitoring species emanating from the 9 mm patch on the sample using LOSMS, while flooding the vacuum chamber with the adsorbing gas (CCl_4 here). Molecules which do not stick, are detected, and after calibration of the detected flux for a known sticking probability (usually $S = 0$ for saturation coverage at room temperature), the absolute sticking probability can be evaluated.

XPS experiments were carried out using beamline UE56/2-PGM-1 on the BESSYII synchrotron in Berlin [9], using a photon energy of 400 eV and a UHV vacuum chamber with an Omicron EA-125HR 125 mm mean radius hemispherical electrostatic analyser equipped with seven-channeltron parallel detection which was mounted at a fixed angle of 60° to the incident X-radiation [10]. Initial XPS results had been obtained using a monochromated X-ray source at Nottingham, but the XPS results presented here (obtained during a structural study of the $:CCl_2$ carbene using photoelectron diffraction at BESSEYII) are clearer due to the higher cross section for ionisation at 400 eV.

The Ag(1 1 1) surface (purchased from Surface Preparation Laboratory [11]) was cleaned by repeated cycles of argon ion bombardment (500 eV, 9 μA, 1800 s) and annealing (833 K); a single bombard/anneal cycle being sufficient after initial, multiple cycle, cleaning following bake-out. The clean surface exhibited a sharp, bright (1×1) LEED pattern, and AES and UPS were free of all features except those due to clean Ag(1 1 1).

3. Results

3.1. Adsorption at 300 K

Fig. 1 shows the UP spectra obtained after exposing clean Ag(1 1 1) to increasing exposures of CCl_4 at 300 K. The clean Ag(1 1 1) spectrum consists of a small Fermi level cut off, three peaks in the d band region between 4 and 7 eV binding energy (BE), and a secondary electron cut off giving a work function of 4.65 ± 0.05 eV (the literature value is 4.74 eV [12]). On adsorbing CCl_4, there is an increase in work function, the sharp peak at 4.9 eV is rapidly quenched, the entire d band intensity reduces, and a small peak grows at 3.2 eV. These results are consistent with dissociative adsorption of the CCl_4 to form a pure chemisorbed adlayer of chlorine.

In Fig. 2 the intensities at 3.2 eV BE (position of the peak characteristic of chemisorbed chlorine [13]) and at 4.9 eV BE (position of the peak characteristic of the clean Ag(1 1 1) surface), and the work function change ($\phi - \phi_{clean}$), are plotted as a function of exposure. All three undergo an initial rapid change during the first 15×10^{-6} mbar s, followed by a flattening of the curves as the surface reaches saturation (exposures $>20 \times 10^{-6}$ mbar s). At saturation ϕ is 1.5 ± 0.1 eV higher than the clean surface value, consistent with the formation of a chemisorbed adlayer of chlorine, and in reasonable agreement with existing data for chlorine chemisorbed on Ag(1 1 1), 1.6 eV [13] and 1.7 eV [14].

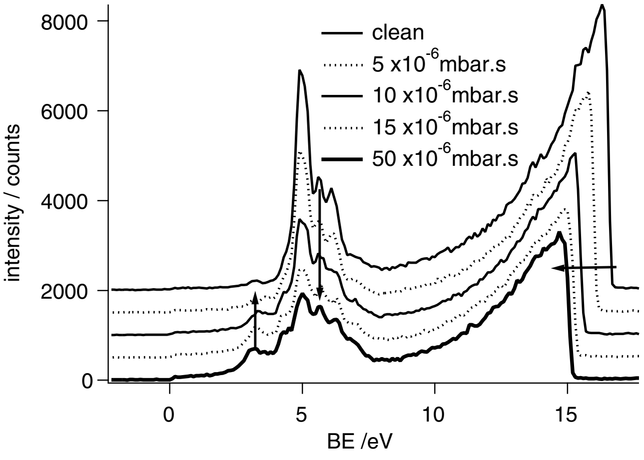

Fig. 1. UPS ($h\nu = 21.2$ eV) of Ag(1 1 1) for increasing doses of CCl_4 at 300 K. Arrows indicate changes for increasing dose. Spectra have been offset by multiples of 500 counts for clarity.