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Surface Science 578 (2005) 27–34
SURFACE SCIENCE
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Adsorption and reaction of methanethiol on Pt(1 1 1)

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Received 17 September 2004; accepted for publication 13 December 2004
Available online 26 January 2005

Abstract

Adsorption and thermal decomposition of H_3CSH on Pt(1 1 1) is studied with temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) with synchrotron radiation. A H_3CSH molecule undergoes dehydrogenation via formation of H_xCS ($x \leqslant 3$) intermediates. The catalytic reactivity of Pt for dehydrogenation, which depends on interaction between the surface and the CH_x moiety of H_xCS, varies with coverage. At large coverage, H_3CSH decomposes through desorbing hydrogen via stepwise dehydrogenation ($H_3CS \rightarrow H_2CS \rightarrow HCS \rightarrow S + C$). H_2CS is proposed to be an intermediate for dehydrogenation of H_3CS below 240 K, and subsequently undergoes disproportionation to form HCS with desorption of CH_4 at 400 K. The HCS species further decomposes to desorb hydrogen at 475 K and to form C and S adatoms; these adatoms show a mixed $(\sqrt{3} \times \sqrt{3})R30°$ and dim $c(2 \times 2)$ LEED pattern at saturation exposure. At small coverage, surface Pt exhibits a catalytic effect on dehydrogenation of H_xCS via interaction of the CH_x moiety with surface Pt atoms. Dehydrogenation of H_3CSH is completed below 370 K and is proposed to form a surface C=S species; this species entirely decomposes to form C and S adatoms at 570 K.
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Keywords: Methanethiol; Dehydrogenation; Pt; XPS; TPD

1. Introduction

Adsorption and thermal decomposition of alkanethiols on platinum metal are of interest from the point of view of industrial importance for several reasons. First, the thermal reaction of alkanethiols on surfaces is associated with poisoning of Pt-based catalysts used to reform hydrocarbons, because these thiols are commonly found in crude oil [1,2]. The second involves preparation of a self-assembled monolayer (SAM) on a metallic surface, which can modify the chemical and physical properties of surfaces and which is potentially adaptable for various applications such as wetting, lubrication and corrosion [3–5]; self-assembled

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doi:10.1016/j.susc.2004.12.029

monolayers of alkanethiols are reported to be formed on the surface of a Pt film with the alkyl chain tilting at an angle 15° [6]. Third, thiols are utilized to stabilize or to functionalize Pt nanoparticles with desired properties [7].

As the simplest sulfur-containing organic molecule, H_3CSH can act as a model compound for the investigation of adsorption and reaction of alkanethiols on a Pt surface. Previous workers have shown that H_xCS species with $x \leqslant 3$ are formed upon adsorption and sequential dehydrogenation of H_3CSH on Pt(111) [8]. Near-edge X-ray absorption fine-structure (NEXAFS) data indicate that the angle of the C—S bond to the surface alters with the extent of dehydrogenation [9,10]. We report here an investigation of the mechanism of adsorption and decomposition of methanethiol on a Pt(111) surface, utilizing thermally programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) techniques; thereby we have elucidated the pathways of the surface reaction. Our spectral results show that dehydrogenation of H_3CSH on Pt(111) depends strongly on the coverage.

2. Experiments

Experiments were performed in a UHV chamber (base pressure $\sim 2 \times 10^{-10}$ Torr) that was equipped with a quadrupole mass spectrometer (EPIC, Hiden) and an electron-energy analyzer (HA100, VSW). A Pt(111) sample was spot-welded on two Ta wires in turn mounted on a copper block. The Pt sample could be cooled to 110 K with liquid nitrogen via conduction through the copper block, and heated resistively. The Pt surface was cleaned through Ar^+-sputtering and then annealed to 1000 K in an oxygen atmosphere ($\sim 10^{-7}$ Torr) to remove residual carbon from the surface. After the surface was further annealed to 1200 K, it exhibited a sharp (1 × 1) LEED pattern and XPS features characteristic of clean Pt, with no evidence for either carbon or oxygen being present. H_3CSH (>99.5%, Matheson) was used in this work without further purification and introduced onto the Pt surface via a tube (1/4-inch stainless steel). During dosing, the partial pressure of H_3CSH was controlled at 5×10^{-10} Torr and the sample was placed ~2 cm before the doser to minimize contamination of the UHV system.

XPS measurements were conducted at the wide-range beamline of National Synchrotron Radiation Research Center in Taiwan; the incident angle of the photon beam was 40° from the surface normal. Emitted photoelectrons were collected with an electron analyzer oriented 15° from the surface normal in an angle-integrated mode. For measurements at varied temperatures, the sample was heated to a desired temperature at a rate 1 K/s and cooled immediately to 110 K, at which time XPS spectra were recorded. H_3CSH are highly sensitive to X-radiation and can undergo photodissociation during XPS measurement. To suppress interference resulting from photodissociation, we completed recording of each XPS spectrum within two minutes, and the probed area of the surface was changed after each XPS measurement. From collected spectra was subtracted a Shirley background with a third-order polynomial on each side of the feature. The resulting data were numerically fitted with Voigt functions for C 1s and S 2p and Doniach–Šunjić functions for Pt 4f [11].

The quadrupole mass filter rendered analysis of desorption products in the TPD measurement. This mass analyzer is enclosed in a differentially pumped cylinder, at the end of which is a skimmer with an entrance aperture (diameter 2 mm). For TPD measurement, the sample surface was placed about 2 mm before the aperture and in line of sight of the mass spectrometer ionizer; TPD spectra were recorded on ramping the sample at a linear rate ~2 K/s.

3. Results and discussion

Fig. 1 shows XPS data recorded for a Pt(111) surface exposed to H_3CSH at 110 K with various exposures. Two S $2p_{3/2}$ components appear at 162.7 and 163.9 eV in order with increasing duration of exposure. The former feature, predominant at small exposures, is attributed to surface methylthiolate (H_3CS), whereas the latter feature is due to chemisorbed H_3CSH. H_3CS is formed on deprotonation of the sulfhydryl group