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The adsorption of ethylene on Au/Pd(1 1 1) alloy surfaces

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Abstract

The adsorption of ethylene on gold–palladium alloys formed on a Pd(1 1 1) surface is investigated using a combination of temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). Various alloy compositions are obtained by depositing four monolayers of gold on a clean Pd(1 1 1) surface and annealing to various temperatures. For gold coverages greater than ~0.7, ethylene adsorbs primarily on gold sites, desorbing with an activation energy of less than 55 kJ/mol. At gold coverages between ~0.5 and ~0.7, ethylene is detected on palladium sites in a π-bonded configuration (with a σ–π parameter of ~0.1) desorbing with an activation energy of between ~57 and 62 kJ/mol. Further reducing the gold coverage leads to an almost linear increase in the desorption activation energy of ethylene with increasing palladium content until it eventually reaches a value of ~76 kJ/mol found for ethylene on clean Pd(1 1 1). A corresponding increase in the σ–π parameter is also found as the gold coverage decreases reaching a value of ~0.8, assigned to di-σ-bonded ethylene as found on clean Pd(1 1 1).

Keywords: Infrared absorption spectroscopy; Chemisorption; Palladium gold alloy; Ethylene

1. Introduction

The synthesis of vinyl acetate monomer (VAM) from ethylene, acetic acid and oxygen is catalyzed by both supported palladium and palladium–gold alloys, where alloying with gold leads to a substantial increase in selectivity from ~85% for pure palladium to approximately 92% for the alloy [1]. The reaction on Pd(1 1 1) has been shown to proceed via a pathway first proposed by Samanos in which ethylene reacts with adsorbed acetate species to form an acetoxyethyl–palladium intermediate, which yields VAM via a β-hydride elimination reaction [see Ref. [2] and references therein]. It has been proposed that reaction proceeds on the alloy at a site consisting of two gold atoms located at diagonally opposite corners of the square unit cell located on a (1 0 0) surface [3]. In order to further understand the effects of alloy formation on this reaction, the following work explores the chemistry of ethylene on gold–palladium (1 1 1) alloy surfaces. This surface was selected for initial study since it has been demonstrated that various alloy compositions can be conveniently obtained by adsorbing ~4 monolayers of gold onto a Pd(1 1 1) surface and annealing to various temperatures to cause gold to diffuse into the palladium substrate. This strategy therefore allows the chemistry of reactants on a relatively large numbers of alloy surface compositions to be compared. In addition, since this alloy system exhibits no additional ordered LEED patterns, it has been suggested that the gold and palladium atoms are randomly distributed at the surface thereby allowing correlations to be made between various surface Au–Pd ensembles and their chemical properties. This strategy was used, for example, to identify the size of the palladium ensemble required for acetylene cyclotrimerization [4].

The ethylene hydrogenation activity of gold–palladium alloys has been investigated theoretically using density functional theory (DFT), where it was found that the formation of the alloy reduced the ethylene heat of adsorption

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[5]. Ethylene bonds in a di-σ configuration on clean Pd(1 1 1) at low-temperatures where low-energy electron diffraction (LEED) measurements and DFT calculations show that it adsorbs at a bridge site [6–9]. The ethylene heat of adsorption is reduced at higher coverages to form π-bonded species. It has also been shown that the presence of sub-surface hydrogen on the Pd(1 1 1) surface induces the formation of π-bonded ethylene and LEED measurements reveal that this occupies an atop site [10,11]. It is therefore anticipated that both electronic and ensemble effects will influence the state of ethylene adsorption on gold–palladium-alloy surfaces.

2. Experimental

The apparatus used to collect reflection absorption infrared spectra (RAIRS) and temperature-programmed desorption (TPD) data have been described in detail elsewhere [12]. Briefly the sample cell used for the infrared experiments is constructed from a 2 3/4 six-way cube, which was oriented to allow infrared radiation to impinge onto the sample at the optimum 80° infrared incidence angle. The cell is attached to the main chamber *via* a gate valve which, when closed, completely isolates the infrared cell from the ultrahigh vacuum chamber and, when open, allows sample transfer into it. Spectra are collected with Bruker Equinox spectrometer, typically for 2000 scans at a resolution of 8 cm^{-1}. TPD data were collected in another chamber that was equipped with a Dichor quadrupole mass spectrometer interfaced to a computer that allowed up to five masses to be monitored in a single experiment. The sample could be cooled to 80 K in both chambers by thermal contact to a liquid-nitrogen-filled reservoir and resistively heated to ~1200 K.

The Pd(1 1 1) single crystal was cleaned using a standard protocol and its cleanliness monitored using Auger spectroscopy and temperature-programmed desorption collected following oxygen adsorption [10]. Gold was evaporated from a small alumina tube [13], which enabled controlled and reproducible evaporation rates to be achieved. In order to precisely control the temperature of the gold, and therefore its evaporation rate, a C-type thermocouple was placed into the gold pellet. The amount of gold deposited onto the surface was monitored using Auger spectroscopy from the peak-to-peak intensities of the Au NVV and Pd MNN Auger features and the monolayer coverage was gauged from breaks in the gold uptake signal. The gold–palladium alloy was formed according to a recipe developed by Lambert et al. [4] by initially adsorbing four monolayers of gold then annealing to various temperatures for a period of five minutes in ultrahigh vacuum to produce the desired Au/Pd atomic ratio on the surface. The sample was then allowed to cool to 80 K, following which ethylene was adsorbed onto the surface at 80 K. The resulting variation in Auger peak-to-peak intensity with annealing temperature was in excellent agreement with previous work [4] and gold coverages are quoted based on this calibration. The ethylene (Matheson, Research Grade) was transferred to glass bottles which were attached to the gas-handling line for introduction into the vacuum chamber.

3. Results

TPD data were collected at a heating rate of 3.7 K/s as a function of ethylene exposure to various gold–palladium alloy surfaces. Only ethylene desorption (27 amu) was detected and no other desorbing species, particularly hydrogen, were found. Ethylene was dosed from a capillary source to minimize the rise in background pressure and the gold–palladium alloy composition, as noted above, was gauged from the Auger spectra using the calibration curve constructed by Lambert et al. [4]. Note that since the electron-based spectroscopies used to construct this calibration may also contain contributions from layers deeper within the selvedge, which presumably contain less gold, it may underestimate the amount of gold in the outer layer. Nevertheless, trends in the variation in gold coverage will correctly track the true values. Data were collected for gold coverages of 0.95, 0.90, 0.73, 0.5, 0.33, 0.17, 0.09, 0.05, and 0.03 monolayers, so that representative data are presented for selected coverages.

TPD data for a gold coverage of 0.73 (27% palladium) are displayed in Fig. 1a. In all cases, the ethylene exposures (in Langmuirs, $1\ \text{L} = 1 \times 10^{-6}$ Torr s) are indicated on the figure. The desorption traces display a feature centered at ~227 K for low exposures with a peak temperature that decreases slightly with increasing ethylene coverage indicating repulsive interactions between adsorbed ethylene species. Note that only very small amounts of ethylene desorb at temperatures above ~150 K at higher gold coverages. Fig. 1b shows the effect of decreasing the gold coverage to 0.33 where ethylene desorbs at ~272 K at low-coverages and shifts and broadens to lower temperatures as the ethylene coverage increases so that, at a saturation ethylene coverage, ethylene desorbs in a broad state centered at ~229 K. Further decreasing the gold coverage to 0.09 (Fig. 1c) results in an increase in the low-coverage ethylene desorption activation energy so that the desorption peak temperature shifts to ~295 K. The ethylene desorption profile at higher exposures is now rather broad with a desorption rate maximum at ~218 K.

The low-ethylene-coverage TPD data are compared for all alloy surfaces in Fig. 2, which displays the desorption profiles as a function of gold coverage, following exposure to 0.25 L of ethylene, where the gold coverages are displayed adjacent to the corresponding spectra. This clearly shows the decreasing trend in desorption temperature with increasing gold coverage. The corresponding desorption activation energies are calculated using the Redhead equation [14] assuming a pre-exponential factor of $1 \times 10^{13}\ \text{s}^{-1}$, and the results are displayed in Fig. 3. These data confirm the decrease in ethylene desorption activation energy with increasing gold coverage. Note that, since ethylene