



The adsorption and reaction of vinyl acetate on Au/Pd(100) alloy surfaces

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ABSTRACT

The surface chemistry of vinyl acetate monomer (VAM) is studied on Au/Pd(100) alloys as a function of alloy composition using temperature-programmed desorption and reflection-adsorption infrared spectroscopy. VAM adsorbs weakly on isolated palladium sites on the alloy with a heat of adsorption of ~55 kJ/mol, with the plane of the VAM adsorbed close to parallel to the surface. The majority of the VAM adsorbed on isolated sites desorbs molecularly with only a small portion decomposing. At lower gold coverages (below ~0.5 ML of gold), where palladium–palladium bridge sites are present, VAM binds to the surface in a distorted geometry via a rehybridized vinyl group. A larger proportion of this VAM decomposes and this reaction is initiated by C–O bond scission in the VAM to form adsorbed acetate and vinyl species. The implication of this surface chemistry for VAM synthesis on Au/Pd(100) alloys is discussed.

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1. Introduction

The synthesis of vinyl acetate monomer (VAM) from ethylene, acetic acid and oxygen on model catalysts has been extensively investigated both experimentally [1–8] and theoretically [2,9]. The reaction pathway has been explored on a Pd(111) model single crystal where it is found that VAM is formed by a reaction between gas-phase ethylene and adsorbed η^2 -acetate species to produce an acetoxyethyl palladium intermediate that yields VAM via a β -hydride elimination reaction [1,2], a pathway originally proposed by Samanos [10]. It has been found that VAM decomposes on clean Pd(111) at the temperatures at which the reaction is carried out [11], but VAM is stabilized by the presence of a saturated overlayer of ethylidyne species produced from ethylene [7,12]. In contrast, on Pd(100), where ethylidyne does not form from ethylene [13], only CO is produced when adsorbed acetate species react with ethylene [8]. This effect is ascribed to the decomposition of the VAM that is formed. However, it has been suggested that the (100) face of gold–palladium alloys is the most active for the catalytic synthesis of VAM [3–5]. It was found that adsorbed acetate species reacted more rapidly with gas-phase ethylene on Pd(100) [8] than on Pd(111) [12], suggesting that it should indeed be more active if the VAM did not decompose. Presumably alloy formation has the effect of preventing the decomposition of any VAM that is produced and it has been suggested that one role of the gold in the alloy is to inhibit carbon accumulation [5,14–18].

Previous studies of the surface chemistry of ethylene [19], VAM [20] and acetic acid [21,22] have been carried out on Au/Pd(111) alloy surfaces [23] to understand the effect of alloying. It was found that the heat of adsorption of ethylene is strongly affected by the formation of a surface alloy, varying from less than ~50 kJ/mol for high gold coverages to ~77 kJ/mol as the gold coverage in the alloy decreases to zero [19]. Alloy formation has a correspondingly strong effect on the chemistry of acetic acid [21] and VAM [20] and results in some palladium segregation to the surface [22].

The gold and palladium atom distributions on the surfaces of Au/Pd(111) alloys are almost random and are dominated by nearest-neighbor interactions between the gold and palladium [24,25] and have been modeled using Monte Carlo methods [25,26]. In contrast, the longer-range interactions found on Au/Pd(100) surfaces lead to the formation of ordered structures [27]. Because of these longer-range interactions, Au/Pd(100) alloys with gold coverages ≥ 0.5 monolayers (ML) contain only isolated palladium atoms with gold atoms as nearest neighbors, while at lower gold coverages, palladium–palladium bridge sites are present. The surface chemistry of acetic acid has been recently studied on Au/Pd(100) alloys [28]. For gold coverages greater than ~0.56 ML, acetic acid desorbs molecularly with an activation energy of ~59 kJ/mol, forming a small amount of η^1 -acetate species. At gold coverages below ~0.56 ML, η^1 -acetate species also form, but then rapidly convert into η^2 -species [16,21,22,29–32] on annealing, and ultimately decompose to desorb CO and hydrogen. It was also found that the presence of co-adsorbed oxygen facilitates acetic acid dehydrogenation favoring η^2 -acetate formation, and the oxygen also serves to stabilize the acetate species.

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These results imply that if VAM formation on (100) surfaces is also initiated by a reaction between ethylene and η^2 -acetate species as found on Pd(111) [1,2], this would occur only for gold coverages below ~ 0.56 ML, and require the presence of palladium–palladium bridge sites on the surface. Co-adsorption of oxygen on the alloy surfaces might facilitate the formation of η^2 -acetate species at higher gold coverages by providing more basic sites on the surface, but no dissociative oxygen adsorption is found on Au/Pd(100) alloys for gold coverages greater than 0.5 ML [33]. Surface science studies suggest, therefore that nearest-neighbor sites are required on both clean and oxygen-covered Au/Pd(100) alloys to activate the acetic acid.

However, since VAM that is formed by reacting ethylene with acetate species on Pd(100) decomposes [8], the formation of a surface alloy may serve to stabilize the VAM that is formed on Au/Pd(100), and this is explored in the following. VAM adsorbs in a flat-lying geometry on clean Pd(111) [11] while, on a Au/Pd(111) it is found that it adsorbs weakly on the gold sites ($\Delta H_{\text{ads}} \sim 55$ kJ/mol) and more strongly on isolated palladium sites ($\Delta H_{\text{ads}} \sim 70$ kJ/mol) [20]. The heat of adsorption of VAM increases with gold coverage and reaches a maximum value of ~ 80 kJ/mol at a gold coverage in the alloy of ~ 0.5 ML. This more stable species is assigned to the formation of distorted VAM in which the acetate group is more remote from the surface due to the rehybridization of the vinyl group [34].

2. Experimental

The apparatus used to collect reflection absorption infrared spectra (RAIRS) and temperature-programmed desorption (TPD) data has been described in detail elsewhere [35]. Briefly RAIR spectra were collected using a Bruker Equinox Fourier-transform infrared spectrometer, typically for 1000 scans at a resolution of 4 cm^{-1} . TPD data were collected at a heating rate of 3.7 K/s in another chamber equipped with a Dichor quadrupole mass spectrometer interfaced to a computer allowing up to five masses to be sequentially monitored in a single experiment as described elsewhere [36]. The sample could be cooled to 80 K in both chambers since it is in thermal contact with a liquid-nitrogen-filled reservoir, and could be resistively heated to $\sim 1200\text{ K}$.

The Pd(100) single crystal was cleaned using a standard procedure and its cleanliness monitored using Auger spectroscopy and TPD collected following oxygen adsorption [37]. Gold was evaporated from a small alumina tube furnace as described in detail elsewhere [38]. The gold coverage on the surface was monitored using Auger and X-ray photoelectron spectroscopies and the gold palladium alloy was formed according to a recipe developed by Lambert et al. [39] and the gold coverages in the resulting alloy were measured using LEIS as described elsewhere [24]. The VAM (Aldrich, 99+% purity) was transferred to a glass bottle, which was attached to a gas-handling line for introduction into the vacuum chamber and was further purified by several freeze–pump–thaw cycles and its purity confirmed by mass spectrometry.

3. Results

TPD profiles were obtained at various masses following the adsorption of VAM at 80 K (using a 1.5 L exposure, $1\text{ L} = 1 \times 10^{-6}$ Torr s, where exposures are not corrected for ionization gauge sensitivities) on a range of Au/Pd(100) alloys. The profile for a completely gold-covered surface yields peaks at 150 and 204 K (data not shown), identical to the desorption temperatures found from gold films on the (111) alloy and assigned to the desorption of VAM multilayers and monolayers, respectively [20]. In this case, only molecular VAM desorption is found.

Fig. 1 displays the desorption spectra for VAM from a Au/Pd alloy with $\theta_{\text{Au}} \sim 0.80$ ML, collected at various masses, which are indicated adjacent to the corresponding desorption profile. This alloy contains

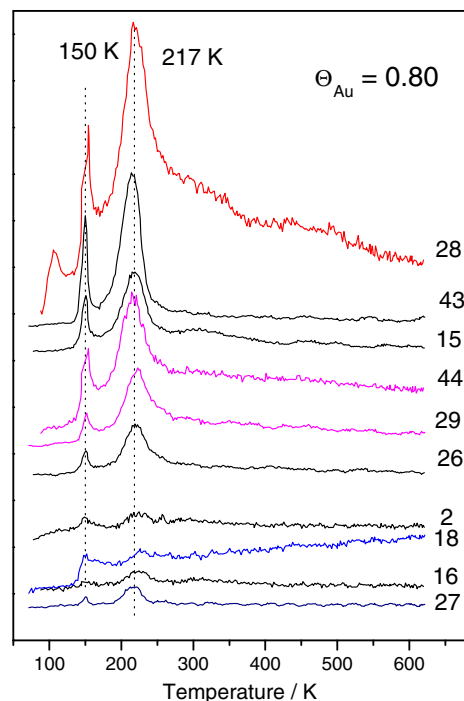


Fig. 1. TPD spectra collected at various masses following adsorption of vinyl acetate (1.5 L) on a Au/Pd(111) alloy with $\theta_{\text{Au}} \sim 0.8$ at 80 K using a heating rate of 3.7 K/s . The monitored masses are indicated adjacent to the corresponding spectrum.

isolated palladium sites with only gold atoms as nearest neighbors [27]. The desorption profiles show a multilayer peak ($\sim 150\text{ K}$) and a feature at $\sim 217\text{ K}$ due to VAM desorption from the surface. A broad and somewhat weaker feature is detected at $\sim 311\text{ K}$ at 15 and 16 amu, along with some additional intensity at 28 amu (CO) in a broad feature above $\sim 250\text{ K}$, indicating that a small proportion of the adsorbed VAM decomposes even at this low palladium coverage ($\theta_{\text{Pd}} = 0.2$ ML).

Decreasing the gold coverage to ~ 0.67 ML, where the surface still contains isolated palladium sites [27], but where the proportion of next-nearest-neighbor sites increases (Fig. 2), further stabilizes the adsorbed VAM so that it desorbs at $\sim 221\text{ K}$. However, the relative integrated intensities at various masses in the $\sim 221\text{ K}$ desorption state no longer agree with the mass spectrometer ionizer fragmentation pattern of VAM indicating some VAM has decomposed. This is confirmed by the intense 2 amu (hydrogen) feature at $\sim 330\text{ K}$ and the desorption of CO (28 amu) at ~ 380 and 460 K . CO desorbs at $\sim 352\text{ K}$ from a Au/Pd(100) alloy with a gold coverage of 0.67 ML [33,40] assigned to CO adsorbed on isolated palladium sites on the surface. This indicates that the CO is formed in a reaction-rate limited surface process. The relatively intense 29 amu fragment of the $\sim 221\text{ K}$ desorption state could be due to acetaldehyde, and the signals at 15 and 16 amu suggest a small amount of methane formation. A broad background in the 18 amu trace may suggest the desorption of water. In addition, a small feature is detected at $\sim 317\text{ K}$ with intensity at 15, 29, 43 and 28 amu.

A similar set of TPD data is displayed in Fig. 3 for a gold coverage of ~ 0.4 ML, where the surface now contains palladium–palladium bridge sites [27]. Multilayer VAM again desorbs at $\sim 150\text{ K}$. Additional features are observed at $\sim 325\text{ K}$, but again the relative intensities in this desorption state do not correspond to VAM, indicating that a portion of the vinyl acetate on this alloy decomposes. In particular, substantial amounts of methane (15 and 16 amu, 337 K), hydrogen (2 amu, 337 K) and carbon monoxide (28 amu, ~ 390 and 460 K) are formed. CO desorbs from an alloy with this composition at ~ 374 (atop sites) and $\sim 480\text{ K}$ (bridge sites) [33,40]. In addition, the broad

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