

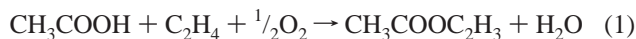
Vinyl Acetate Formation by the Reaction of Ethylene with Acetate Species on Oxygen-Covered Pd(111)

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Received September 3, 2004; E-mail: wtt@uwm.edu

The palladium-catalyzed synthesis of vinyl acetate monomer (VAM) from acetic acid, ethylene, and oxygen,



was first discovered some 30 years ago,¹ and currently approximately 3000 metric tonnes are produced annually by this reaction.² Complete combustion to carbon dioxide also occurs, where both ethylene and acetic acid have been implicated as the sources of CO₂.^{3–5} Formation of palladium/gold alloys results in an increase in selectivity,⁶ possibly due to an enhanced stabilization of the surface acetate species.⁷ However, despite the importance of this reaction, there is currently little fundamental understanding of the heterogeneous reaction pathway. Previous studies of the adsorption of acetic acid on Pd(111) have identified both η^1 - and η^2 -acetate species.^{8,9} It has been suggested, based on in situ infrared spectroscopic experiments, that the η^1 -acetate species is the active form of acetic acid on the surface of an active catalyst.¹⁰ However, solution-phase reactions between η^2 -acetates and ethylene yielding vinyl acetate have been found,¹¹ so that the nature of the active, acetic-acid-derived species on the catalyst surface remains an open question. Ethylene adsorbs in a π -bonded configuration on oxygen-covered Pd(111).¹²

In the following we report the first observation of the reaction between gas-phase ethylene and acetate species adsorbed on oxygen-covered Pd(111), which is likely to be the rate-limiting step in the overall catalytic pathway.⁷ The model acetate plus oxygen-covered catalyst surface is prepared by exposing a Pd(111) single crystal to oxygen at 300 K (100 L, 1 L = 1×10^{-6} Torr·s) to form a (2×2) overlayer,¹³ where the presence of the (2×2) overlayer is confirmed using low-energy electron diffraction (LEED). This surface was then exposed to acetic acid (5 L) at 300 K to form a saturated overlayer of acetate species. The saturation acetate coverage, measured from the integrated intensity of the C 1s X-ray photoelectron (XPS) signal, is 0.31 ± 0.02 monolayer (where coverages are ratioed to the atom site density on the Pd(111) surface). While the acetate and oxygen coverages under catalytic conditions are not known, and indeed will vary with temperature and reactant pressures, both species are likely to be present so that this model surface is a reasonable starting point for mechanistic studies. This surface is then pressurized with ethylene, which is directed onto the surface using a dosing tube to provide an enhanced pressure at the surface, while minimizing the background pressure in the ultrahigh vacuum chamber. The nature of the surface is then scrutinized using reflection-absorption infrared spectroscopy (RAIRS) to monitor the time-dependent variation in the coverage of the surface species. Gas-phase products are monitored by a mass spectrometer in a separate experiment while the sample temperature is ramped. The RAIRS and temperature-programmed reaction (TPR) experiments and equipment have been described in detail elsewhere.¹⁴

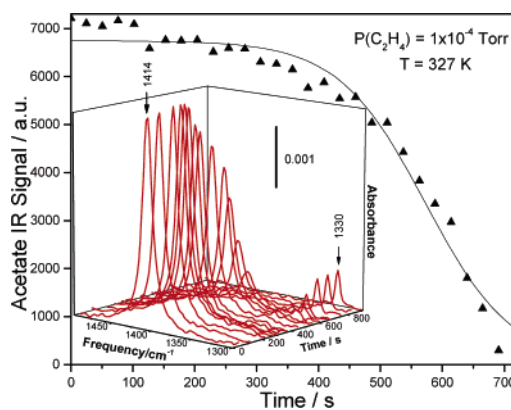


Figure 1. Plot of the integrated intensity of the 1414 cm⁻¹ feature, due to acetate species, as a function of time. The lines plotted through these data are the results of a kinetic fit (see text). Shown also is the time sequence of infrared spectra of a saturated overlayer of acetate species on Pd(111)–(2×2)O pressurized by 1×10^{-4} Torr of ethylene at 327 K.

The time evolution of the RAIRS spectra of acetate on Pd(111)–(2×2)O after allowing a beam of gas-phase ethylene to impinge onto the surface is shown in Figure 1. The beam pressure in this case was measured to be 1×10^{-4} Torr, and the sample was held at 327 K. The effective ethylene pressure at the sample was measured by monitoring the uptake of carbon monoxide using RAIRS,¹⁵ compared with the known adsorption kinetics of CO on Pd(111).¹⁶ Under the conditions used in these experiments, no gas-phase ethylene was detected in the infrared spectrum. The spectrum for time $t = 0$ (prior to ethylene exposure) shows an extremely intense feature at 1414 cm⁻¹ assigned to the symmetric acetate OCO stretching mode. Weaker features detected at 677 and 2932 cm⁻¹ (not shown) are assigned to $\delta(\text{OCO})$ and methyl stretching modes, respectively.^{8,9} The intense 1414 cm⁻¹ feature attenuates following ethylene exposure. Control experiments carried out at this temperature in the absence of gas-phase ethylene, or in the presence of CO, show no change in the intensity of the 1414 cm⁻¹ mode, indicating that acetate removal is caused by reaction with ethylene. As the surface becomes depleted of acetate species, another feature grows at 1330 cm⁻¹ (Figure 1). Such a feature has been assigned previously to ethylidyne (CH₃–C≡) species.¹⁴ This assignment was confirmed by demonstrating that the 1330 cm⁻¹ peak disappeared at the same temperature at which ethylidyne species, intentionally grown on Pd(111) by exposure to ethylene, were thermally removed.

Experiments were carried out to show that the intensity of the 1414 cm⁻¹ acetate mode varies linearly with acetate coverage, and it has been shown previously that the intensity of the 1330 cm⁻¹ ethylidyne feature similarly varies linearly with coverage. This allows the time evolution of the acetate and ethylidyne coverages to be plotted, and the results are shown in Figure 1. Varying the ethylene pressure demonstrated that the available surface is saturated

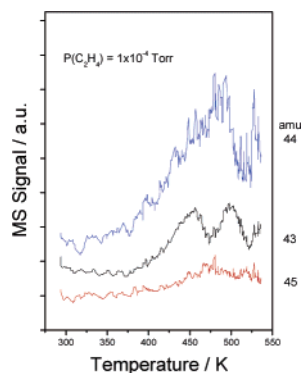


Figure 2. TPR data collected at 44 (CO_2), 43 (vinyl acetate), and 45 (acetic acid) amu for a Pd(111)-(2 \times 2)O surface saturated with acetate species with a beam of ethylene impinging onto the surface with an effective pressure of $\sim 1 \times 10^{-5}$ Torr.

by ethylene at a beam pressure of 1×10^{-4} Torr, since neither lowering the ethylene pressure to 2×10^{-5} Torr nor increasing it to 2×10^{-3} Torr changed the shape of the curves shown in Figure 1.

To model the removal kinetics, the reaction between ethylene and an acetate species is taken to be first order in the coverage of each reactant and therefore second-order overall, giving a rate of acetate removal as

$$-\frac{d\Theta}{dt} = k\Theta\Theta_e \quad (2)$$

where Θ is the relative acetate coverage and k the reaction rate constant. This reaction can, in principle, proceed via the initial formation of a vinyl species, which reacts directly with the acetate,¹⁸ or alternatively by reaction between ethylene and the acetate where VAM is formed by a final hydrogen elimination step.¹⁹ Θ_e therefore refers to the relative coverage of ethylene-derived species. It is assumed that adsorbed acetate species block ethylene adsorption and, with the saturation acetate coverage given by Θ_0 , eq 2 becomes

$$-\frac{d\Theta}{dt} = k\Theta\Theta_e^0(\Theta_0 - \Theta) \quad (3)$$

where Θ_e^0 is the saturation coverage of ethylene-derived species. At $t = 0$, $\Theta = \Theta_0 - \delta$, where δ is an initial "defect" coverage to allow ethylene to adsorb on the initially acetate-saturated surface, so that eq 2 can be integrated directly by assuming that $\delta \ll \Theta_0$ to yield

$$\Theta = \frac{\Theta_0}{1 + (\delta/\Theta_0)e^{k't}} \quad (4)$$

where $k' = k\Theta_e^0$. A fit to eq 4 is shown as a solid line in Figure 1, where the agreement is excellent and yields values of $\delta = (3 \pm 2) \times 10^{-4}$ monolayer and $k' = (1.4 \pm 0.1) \times 10^{-2} \text{ s}^{-1}$.

A TPR experiment was carried out in which a beam of ethylene ($P = 1 \times 10^{-5}$ Torr) was incident on an acetate-saturated Pd(111)-(2 \times 2)O surface while the sample temperature was ramped at 1.7 K/s. The results are displayed in Figure 2, monitoring fragments at 44, 43, and 45 amu with a quadrupole mass spectrometer. The mass spectrum of vinyl acetate exhibits an intense feature at 43 amu so

that the 43 amu trace in Figure 2 is consistent with the desorption of vinyl acetate. Some CO_2 (44 amu) also desorbs due to acetate decomposition. The very weak 45 amu signal indicates that essentially no acetic acid desorbs from the surface, further confirming that the 43 amu signal is due to vinyl acetate formation, in accord with eq 1.

These results indicate that ethylene can react rapidly with surface acetate species adsorbed on oxygen-covered Pd(111) to form vinyl acetate, strongly suggesting that the catalytic synthesis of vinyl acetate proceeds via a surface η^2 -acetate intermediate. It should be emphasized that this does not preclude the participation of other surface intermediates in the catalytic reaction under realistic conditions but indicates that a surface η^2 -acetate species is a likely candidate for the surface acetic-acid-derived reactant in the synthesis of vinyl acetate. The data presented here do not allow us to establish which of the proposed mechanisms mentioned above, either ethylene or vinyl reaction with acetate, operates. However, the ability to measure the rate of an elementary step in this reaction under ultrahigh vacuum conditions will allow this question to be addressed.

It is evident from Figure 1 that ethylidyne is formed on the surface as it becomes depleted of acetate species, and is most likely not involved in the formation of VAM. Ethylidyne species thermally decompose to yield hydrogen and carbon at ~ 450 K on clean Pd(111), which will oxidize to form water and carbon dioxide, respectively.¹⁷ It has recently been suggested that ethylene is the source of total combustion products,¹⁷ and the detection of ethylidyne species suggests a possible route for this reaction. The TPR data of Figure 2 also suggest that CO_2 can form from the decomposition of the acetate, and presumably the relative contribution of ethylene combustion and acetate decomposition to the formation of CO_2 will depend on the rate at which the acetate species react with ethylene compared to their decomposition rate.

Acknowledgment. We gratefully acknowledge support of this work by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Grant No. DE-FG02-92ER14289.

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JA044641W