Reaction Mechanisms

Elucidation of the Reaction Mechanism for the Palladium-Catalyzed Synthesis of Vinyl Acetate**

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Two basic mechanisms have been proposed for the palladium-catalyzed synthesis of the vinyl acetate monomer (VAM) from acetic acid, ethylene, and oxygen [Eq. (1)]:[1]

$$CH_3COOH + C_2H_4 + {}^1\!/\!_2O_2 \rightarrow CH_3COOC_2H_3 + H_2O \qquad (1)$$

The first, suggested by Samanos et al., involves the coupling of ethylene directly with chemisorbed acetate.[2] The resulting acetoxyethyl–palladium intermediate then undergoes β-hydride elimination to form vinyl acetate. Alternatively, ethylene could first dehydrogenate to form a vinyl–palladium intermediate, which then couples with an acetate species adsorbed on the surface to form the VAM directly. This latter mechanism was proposed by Moiseev et al.[3,4] as well as by Nakamura and Yasui.[5] We have recently shown that ethylene in the gas phase reacts with a model-catalyst surface of η^2-acetate moieties adsorbed on a Pd(111) surface precovered with a (2×2) oxygen overlayer to form the VAM,[6] thus implying that the acetate species is the precursor to formation of the VAM.

The structures of the adsorbed η^2-acetate[7] and ethylene[8] species were determined separately on a Pd(111) surface by using low-energy electron diffraction (LEED) and reflection-absorption IR spectroscopy (RAIRS),[6–9] which showed that both species adsorb on the bridge site. Herein, we discuss the investigation into the nature of the reaction pathway by using isotopically labeled reactants, which allowed the mechanism for the formation of the VAM to be unequivocally identified. The RAIRS experiments were performed in an ultrahigh vacuum apparatus; the experimental procedure has been described in detail elsewhere.[10] Kinetic measurements were typically carried out by the collection of spectra over 100 scans, which is a relatively short procedure that took 25 seconds because of the large intensity of the asymmetric vibrational mode of the acetate moiety (O-C-O) at 1414 cm^{-1}.[6] Some experiments were carried out with a larger number of scans to yield spectra with better signal-to-noise ratios and, therefore, allow additional surface species to be identified. A flux of ethylene impinged onto the sample from a collimated dosing source to obtain an enhanced flux at the Pd(111) single-crystal surface while the background pressure was minimized.[6] C_2H_4 (Matheson, Research Grade), acetic acid (Aldrich, 99.99+%), C_2D_4 (CIL, 98% D), CD_2CH_2 (CDN, 99% D), CHDCHD (CDN, *cis*/*trans* mixture, 99% D), and $^{18}O_2$ (CIL, 95% $^{18}O_2$) were transferred into glass bottles, which were attached to the gas-handling line for introduction into the vacuum chamber.

It has been shown previously that acetate species adsorbed on a Pd(111)–O(2×2) surface undergoes reaction with ethylene in the gas phase to yield the VAM.[6] The experimental titration curves obtained with acetate species can be explained by using a procedure described previously,[6] in which it was assumed that adsorbed ethylene underwent reaction with the acetate species and that ethylene adsorption was blocked by the acetate species. Acetate species adsorbed on clean Pd(111) surfaces (namely, in the absence of the (2×2) oxygen overlayer) are also removed by reaction with ethylene and also can be analyzed by using the same procedure used to reproduce the kinetic data for the oxygen-covered Pd(111) surface; furthermore, these acetate species yield similar rate constants to those found for reactions on the oxygen-covered surface, and therefore the presence of coadsorbed oxygen does not substantially affect the reaction kinetics.

A series of IR spectra for the reaction of the acetate species on a clean Pd(111) surface was collected just after the acetate moieties had been completely removed using C_2H_4, C_2H_4 (on an ^{18}O-covered surface), and C_2D_4 (Figure 1). The spectrum of CO on the Pd(111) surface is shown for comparison (Figure 1a). The CO exposure was selected to

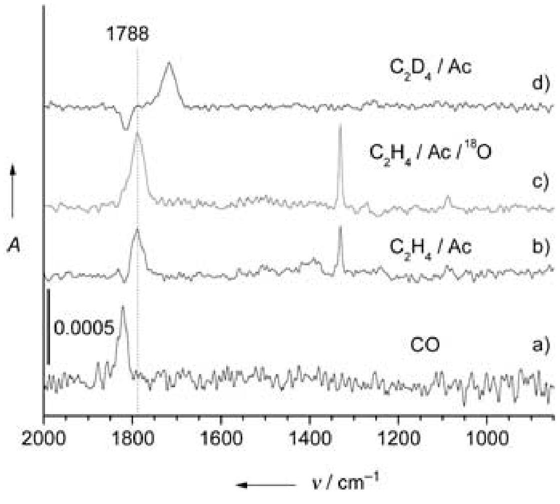

Figure 1. IR spectra of the reaction of acetate species with ethylene at 327 K after the acetate species had been removed. Spectra are given for the reactions of: b) C_2H_4 on an acetate-covered Pd(111) surface, c) C_2H_4 on an acetate-covered Pd(111)–^{18}O(2×2) surface, and d) C_2D_4 with a acetate-covered Pd(111) surface. a) IR spectrum of CO on a Pd(111) surface is shown for comparison. Ac = acetate.

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yield a similar intensity of signals to those produced by the reaction between ethylene and the adsorbed acetate species, thus indicating that none of the signals result from CO adsorbed from the background. The signals at 1330 and 1090 cm^{-1} in the spectra in Figure 1b and c arise from the ethylidyne species.[6] Deuterated ethylidyne has very weak IR features and is not detected in the spectrum in Figure 1d. The spectrum in Figure 1b demonstrates that surface oxygen does not participate in the formation of surface species. A signal is evident at 1788 cm^{-1} following the reaction with C_2H_4, whereas another is present at 1718 cm^{-1} following the reaction with C_2D_4. A deuterium isotope effect is measured which indicates that C_2D_4 undergoes reaction with the acetate species approximately six times more slowly than with C_2H_4 (see below). To establish whether the signal at 1718 cm^{-1} results from an isotopic shift of the absorption at 1788 cm^{-1} or a different species and to help establish the nature of the species that gives rise to the signal at 1788 cm^{-1}, both perdeuterated and undeuterated vinyl acetate were adsorbed on an ethylidyne-saturated Pd(111) surface at 300 K (data not shown). The RAIRS spectra revealed that the VAM exhibits a single signal at approximately 1780 cm^{-1} for both the perdeuterated and undeuterated vinyl acetate. The signal at 1718 cm^{-1} evidently does not result from either the vinyl acetate or the monodentate acetate species,[11,12] as the latter would have also been observed during reaction with C_2H_4. The presence of this signal does, however, provide a clue to the reaction pathway. The only species expected to be present on the surface in the pathway proposed by Moiseev et al.[3] are ethylene, the vinyl and acetate moieties, and vinyl acetate. Once the characteristic frequencies of these species are considered, however, it is clear that the signal at 1718 cm^{-1} does not arise from any of these.[6–9] The species present in the pathway proposed by Samanos et al. are ethylene, acetate, vinyl acetate, and the acetoxyethyl–palladium intermediate that results from insertion of ethylene into the acetate–Pd bond. Again bearing in mind their characteristic frequencies, the signal at 1718 cm^{-1} does not arise from ethylene,[9] acetate,[6,11,12] or vinyl acetate.

Density functional theory (DFT) calculations demonstrate that an acetoxyethyl–palladium intermediate has a C=O stretching frequency approximately 80 cm^{-1} lower than that of vinyl acetate. The calculations were carried out by using periodic plane-wave DFT calculations with the $DMOL^3$ code[13] and the Perdew–Wang91[14] form of the generalized gradient approximation. Pure ethyl acetate has a C=O stretching frequency substantially lower than that of vinyl acetate,[15] and a proposed acetoxyethyl–palladium species on a Pd–Al_2O_3 surface has a characteristic frequency of well below 1788 cm^{-1}.[16] The signal at 1718 cm^{-1} is, therefore, assigned to an acetoxyethyl–palladium intermediate, the presence of which can only be rationalized on the basis of the pathway proposed by Samanos et al.,[2] where this intermediate decomposes to form the VAM by β-hydride elimination. The decomposition rate of the acetoxyethyl–palladium intermediate will be slowed substantially by deuteration at the β position, thus accounting for the appearance of this intermediate when C_2D_4 reacts with the surface acetate species. Reaction with C_2H_4 results in a faster decomposition rate of the intermediate such that insufficient quantities accumulate to allow detection by IR spectroscopy.

In view of this isotope effect, the acetate species on the Pd(111) surface was treated with C_2D_4, CH_2CD_2, and CHDCHD, and the resulting plots of the acetate coverage versus time are displayed, along with the data for C_2H_4, in Figure 2. There are substantial differences in the reaction rates between C_2H_4 and C_2D_4 which indicate, as noted above, that hydrogen is involved in the rate-limiting step. Interestingly, the reaction rates for [D_2]ethylene depend on the position of the deuterium isotope: the reaction is slower for the 1,1-dideuterated reactant than for 1,2-dideuteroethylene. This observation allows us to exclude the model proposed by Moiseev et al. immediately as, in this case, the rate-limiting step, which involves hydrogen, must be hydrogen abstraction from ethylene to form the vinyl species. An analysis of the experimental data[6] (Figure 2) yields $k_H/k_D \approx 6$, which is a reasonable value for a primary isotope effect. In the case of the reaction with [D_2]ethylene, and according to the pathway of Moiseev et al., the rate constant should be $(k_H + k_D)/2$ irrespective of the location of the deuterium atom, thus yielding an isotope effect of $2/(1+(k_D/k_H)) \approx 1.7$.

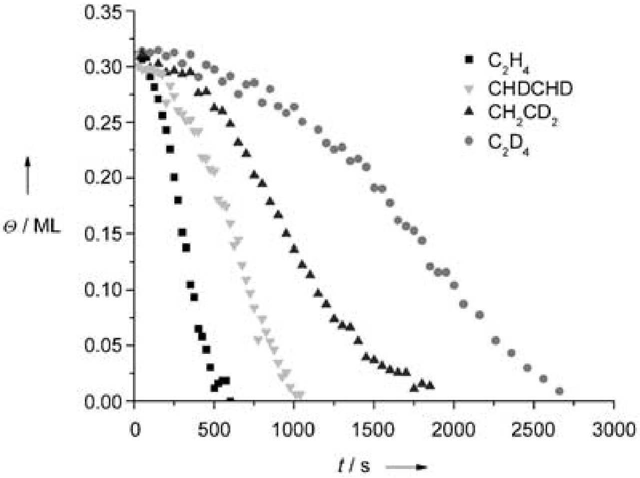

Figure 2. Plot of time versus coverage Θ, as measured from the intensity of the signal at 1414 cm^{-1} of the acetate species, for the reaction of C_2H_4 (■), CH_2CD_2 (▲), CHDCHD (▼), and C_2D_4 (●) carried out with the acetate species adsorbed on a Pd(111) surface, with an ethylene pressure of 2×10^{-7} Torr, and at a reaction temperature of 327 K.

At first sight, a similar effect should occur with the model proposed by Samanos et al. In the case of the reaction with CH_2CD_2, there is an equal probability of CH_2 or CD_2 units being in the β position in the acetoxyethyl–palladium intermediate, thus yielding an isotope effect of approximately 1.7; whereas there will always be a CHD unit at the β position in CHDCHD, thus yielding a similar isotope effect of approximately 1.7. If it is assumed that the acetoxyethyl–palladium intermediate blocks the adsorption of ethylene, however, any intermediates formed from CH_2D_2, which has two deuterium atoms at the β position, will decompose more slowly than those with hydrogen atoms at the β position, thus blocking ethylene adsorption and lowering the reaction rate. For the reaction with CHDCHD, hydrogen atoms will always be present at the β position, so the intermediate decomposes more rapidly, which results in decreased blocking of ethylene adsorption by the intermediate. These observations suggest that reaction with CH_2CD_2 should be slower than with CHDCHD, as was found experimentally (Figure 2). This proposal is in accord with the identification of the acetoxyethyl–palladium intermediate in the reaction between the acetate species and C_2D_4 (Figure 1). In this case, there is always a deuterium atom at the β position which results in slower decomposition of the acetoxyethyl–palladium intermediate, thus allowing it to be detected by IR spectroscopic analysis. The detection of this species confirms that sufficient quantities can accumulate on the surface to affect the relative reaction rates of the 1,1- and 1,2-dideuteroethylenes, as found by the data shown in Figure 2.

Thus, the experimental results provide clear evidence that the reaction of ethylene with the acetate species proceeds through the pathway proposed by Samanos et al.,[2] that is, by insertion of ethylene into an adsorbed acetate species and subsequent β-hydride elimination to form vinyl acetate. First, when a reaction is carried out using C_2D_4, a vibrational mode at 1718 cm^{-1} is identified, which is assigned to the acetoxyethyl–palladium intermediate (Figure 1). Second, the differences in the reaction rates for CHDCHD and CH_2CD_2 can only be rationalized by the route of Samanos et al.; therefore, the reasonable assumption can be made that the acetoxyethyl–palladium intermediate blocks the adsorption of ethylene (Figure 2). Our mechanism is essentially the same as that observed for the stoichiometric oxidation of ethylene to the VAM by soluble palladium acetate.[17] Although it was a reasonable proposal that the surface-mediated reaction would be parallel to that of the related solution-phase process, the distinctly different reactivity of ethylene towards the two palladium species made disparate mechanisms plausible. Now that the intermediacy of an acetoxyethyl–palladium species in the surface-mediated process has been established, questions still remain that concern the geometry of each step. Whether the insertion of ethylene proceeds in an *anti* mode, as observed in the solution phase,[17] or by a *syn* process, which is apparently more appropriate for a surface, will be investigated in future studies.

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