

Hydrogen Bonding in Carboxylic Acid Adlayers on Pd(111): Evidence for Catemer Formation[†]

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The adsorption of acetic acid and propanoic acid was studied on the Pd(111) surface in order to gain insights into the extent of hydrogen bonding present in carboxylic acid adlayers. In the solid phase, acetic acid is known to crystallize in hydrogen-bonded catemers of the form $(\text{CH}_3\text{COOH})_n$, while propanoic acid crystallizes as dimers of the form $(\text{CH}_3\text{CH}_2\text{COOH})_2$. However, on the clean Pd(111) surface both of these adsorbates formed hydrogen-bonded catemers as indicated by the reduction of the $\nu(\text{OH})$ vibration frequency to ca. 2550 cm^{-1} . Acetic acid catemers decomposed near 200 K to produce molecular acetic acid which either desorbed or dissociated to form surface acetates. These acetates reacted via two parallel pathways: hydrogenation to acetic acid and decarboxylation. The decomposition of propanoic acid catemers occurred via sequences analogous to those observed for acetic acid. Propanoates derived from the propanoic acid adlayer underwent either hydrogenation to propanoic acid at 280 K or decarboxylation at 355 K. The observation of catemer formation from both acetic and propanoic acids suggests that adsorbed monolayers may differ from crystalline solids in their hydrogen-bonding characteristics.

Introduction

Intermolecular hydrogen bond formation is readily observed for virtually all carboxylic acids. At low pressures, gaseous carboxylic acids exist predominantly as monomers; however, dimerization of carboxylic acid molecules due to intermolecular hydrogen bonding increases at higher pressures. Liquid-phase carboxylic acids exhibit a preference for dimer formation. The degree of hydrogen-bonding-induced oligomerization for crystalline carboxylic acids is determined by the nature of the alkyl substituent on the carboxyl group. Both formic acid and acetic acid form hydrogen-bonded polymers in the crystalline phase, as established by a combination of crystallography and vibrational studies.¹⁻⁶ In this hydrogen-bonding arrangement, the carboxyl group of the acid monomer is linked to two other molecules by single hydrogen bonds, forming a spiral chain of hydrogen-bonded acid molecules of the form $(\text{RCOOH})_n$. This packing geometry is referred to as the catemer motif for carboxylic acid crystallization. In contrast, for higher molecular weight carboxylic acids the energetics of crystal packing are such that dimerization is preferred over catemerization.⁷⁻⁹ Dimerization of carboxylic acids is favored by repulsive van der Waals forces between the alkyl substituents on

the carboxylic acid molecules; these forces render catemerization less favored thermodynamically.⁷⁻⁹ For example, the ethyl substituent of propanoic acid is sufficiently large that this carboxylic acid crystallizes as dimers, as established by X-ray diffraction studies.¹⁰ Generally, carboxylic acids larger than propanoic acid will also crystallize as dimers.⁷⁻⁹

Among the most powerful techniques sensitive to hydrogen bonding in carboxylic acids are vibrational spectroscopies. IR and Raman studies have demonstrated that the OH stretching frequency of acetic acid monomers is 3577 cm^{-1} .¹¹ Similar frequencies are observed for the $\nu(\text{OH})$ mode of other carboxylic acid monomers. The weak hydrogen-bonding interaction observed for gas-phase acetic acid dimers shifts the OH stretch to 3193 cm^{-1} .^{12,13} For crystalline propanoic acid dimers, the $\nu(\text{OH})$ mode appears as a broad feature centered near 3000 cm^{-1} .¹⁴ The OH stretch of carboxylic acid catemers is also broadened by hydrogen-bonding interactions but occurs at lower frequencies than observed for dimers due to the more extensive hydrogen bonding present in catemer species. IR studies have observed the $\nu(\text{OH})$ mode of acetic acid catemers in the solid state as a broad peak centered at 2875 cm^{-1} .⁶ As discussed by Novak,¹⁵ the frequency of the OH stretch of hydrogen-bonded species provides an indication of the strength of the hydrogen-bonding interaction. Weak hydrogen bonds result in a smaller decrease in the OH stretching frequency from the gas-phase value than do stronger hydrogen bonds. On the basis of the classification of Novak, the strength of the hydrogen bond in carboxylic acid dimers can be classified as weak to intermediate, while the strength of the hydrogen bond in acetic acid catemers can be classified as intermediate to strong. The enthalpy of formation of weak hydrogen

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bonds is less than 5 kcal/mol, while the enthalpy of formation of strong hydrogen bonds is greater than 8 kcal/mol.¹⁵

Just as vibrational spectroscopies have proven indispensable in studying hydrogen bonding of carboxylic acids in the crystalline phase, vibrational studies of carboxylic acids adsorbed on metal surfaces using high-resolution electron energy loss spectroscopy (HREELS) can provide insights into the intermolecular interactions which control reaction selectivity. The large shifts in the OH stretching frequency observed for varying degrees of hydrogen bonding of carboxylic acids can be easily detected in HREELS experiments. Further, studying both carboxylic acids which crystallize as catemers (such as acetic acid) and those which crystallize as dimers (such as propanoic acid) allows a systematic analysis to be made of the influence of the metal surface in altering these bonding interactions. Previous studies have suggested that the presence of hydrogen bonding can influence the selectivity of carboxylic acid reactions on group VIII metal surfaces. TPD studies following formic acid¹⁶ and acetic acid¹⁷ adsorption on Ni(110) reported different reaction selectivities for the decomposition of monomers and dimers.

Experimental Section

The experiments were conducted in two separate stainless steel ultra-high-vacuum chambers which have been described previously.^{18,19} The Pd(111) crystal was polished by using standard metallographic techniques, finishing with 1- μ m diamond paste. After insertion into the vacuum chamber, the Pd(111) crystal was cleaned via cycles of Ar⁺ bombardment, annealing at 1000 K under vacuum, and annealing at 900 K under 10⁻⁸ Torr of flowing O₂. The Pd(111) crystal was cleaned with the above procedure until no impurities were observed with either AES or HREELS.

For a typical TPD experiment in this study, the adsorption temperature was 170 K. TPD spectra were collected with the aid of an IBM personal computer, which allowed up to eight different *m/e* ratios to be monitored simultaneously. The heating rate of the crystal was controlled by a programmable power supply interfaced with the computer. A linear temperature ramp of 10 K/s was used in all TPD experiments described below. The TPD spectra were corrected for mass spectrometer sensitivity by using standard formulas.²⁰ Absolute coverages were determined by comparison with the peak area for desorption of CO adsorbed in the ($\sqrt{3} \times \sqrt{3}$)R30° overlayer, which has an ideal coverage of one-third monolayer. HREEL spectra presented below were obtained by using procedures similar to those described previously.¹⁹ Spectra were recorded with a beam energy of 5 eV, and the fwhm of the elastically scattered peak was 56–64 cm⁻¹.

The carboxylic acids used in these experiments were stored on the dosing manifold described previously.¹⁸ Samples of CH₃COOH (Fisher, 99.7%), CH₃COOD (Chemical Dynamics, 99.5% D), CD₃COOD (Chemical Dynamics, 99.5%), and CH₃CH₂COOH (Aldrich, 99+%) were transferred directly from the reagent bottles to the sample reservoirs. All samples were purified by multiple freeze–pump–thaw cycles, and the purity was checked by mass spectrometry. The carboxylic acids were admitted to the chamber through a 1.6-mm needle that served as a molecular beam doser. Unless otherwise mentioned, all doses were delivered with a carboxylic acid pressure of 100 mTorr at 298 K in the dosing line. The pressure in the vacuum chamber rose no higher than 10⁻⁹ Torr during the carboxylic acid exposure and rapidly returned to 10⁻¹⁰ Torr upon completion of the dose.

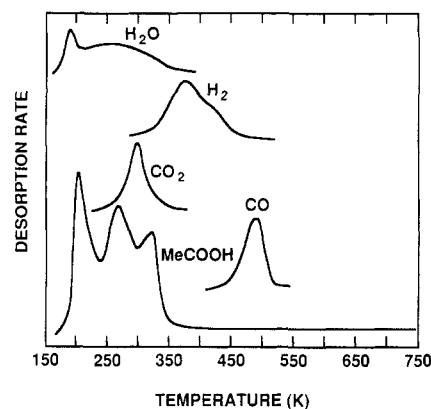


Figure 1. TPD spectrum following a saturation exposure of CH₃COOH on Pd(111) at 170 K.

Results

Acetic Acid. The adsorption of acetic acid on the Pd(111) surface at 170 K produced predominantly molecular species, although some activity was observed for dissociative adsorption to generate acetate species. The dissociated state was populated at low coverages, while molecular adsorption was prevalent at higher coverages. Quantitative analysis of the desorption and decomposition products indicated that the total number of acetic acid molecules adsorbed at 170 K reached a saturation value of 5×10^{14} cm⁻², i.e., one-third monolayer with respect to the surface Pd atom density. Thus, contributions from multilayer states to the TPD and HREEL spectra of this work can be ruled out. Following a saturation exposure of acetic acid on the clean Pd(111) surface, acetic acid desorption occurred at 205, 270, and 330 K, as shown in Figure 1. A portion of the acetic acid adlayer underwent reactions which produced CO₂ (*T_p* = 300 K), H₂ (*T_p* = 375 K), and CO (*T_p* = 490 K). The observation of CO₂ desorption at 300 K indicates that acetate decarboxylation occurred at this temperature, analogous to the behavior observed for formate species on Pd(111).²¹ A similar acetate decomposition reaction was also observed following acetic acid adsorption on the oxygen-dosed Pd(111) surface.²²

The decarboxylation of acetate species would be expected to release C₁ hydrocarbon species to the surface. However, methane desorption was not observed in the acetic acid TPD experiments. In contrast, the formation of methane via the hydrogenation of adsorbed methylene (CH₂) species has previously been observed in TPD experiments with ethanol¹⁸ and acetaldehyde²³ on Pd(111).

The desorption of H₂ occurred with a maximum rate at 375 K in these experiments, and the onset of desorption for this product was delayed until 290 K. The peak shape and desorption temperature for this H₂ product suggest contributions from predominantly reaction-limited H₂, although a small amount of desorption-limited H₂ may be present. The evolution of desorption-limited hydrogen occurs between 320 and 350 K,²⁴ while reaction-limited hydrogen produced by the decomposition of C₁ hydrocarbon species desorbs near 400 K.¹⁸ The observation of reaction-limited H₂ products indicates that decomposition pathways are prevalent for the C₁ hydrocarbon species produced by acetate decarboxylation. The decomposition of these hydrocarbons at 400 K produced

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a carbon adlayer that remained upon completion of the TPD experiments. This carbon adlayer was removed by cycles of O_2 adsorption at 300 K, followed by flashing the crystal to 1000 K. This procedure was repeated until no desorption of carbon oxides (i.e., CO or CO_2) was observed, and neither HREELS nor AES detected the presence of adsorbed carbon.

Following a saturation exposure of acetic acid on the clean Pd(111) surface, three distinct acetic acid desorption states were resolved in TPD experiments. Desorption of acetic acid at 205 K can be attributed to the evolution of molecular species, as indicated by HREELS experiments described below. Multilayer adsorption of acetic acid at 170 K can be ruled out based upon the quantitative coverage values from TPD and upon the observation that preadsorption of one-quarter monolayer of oxygen atoms completely suppresses acetic acid desorption between 170 and 300 K.²² The activation energy for desorption from this state was calculated to be 11.9 kcal/mol, using the method of Redhead²⁵ and assuming first-order desorption with a frequency factor of 10^{13} s^{-1} . The two higher temperature acetic acid desorption states at 270 and 330 K resulted from the hydrogenation of surface acetate species. Adsorbed carboxylate species undergo hydrogenation reactions on the Pd(111) surface at temperatures greater than 250 K, provided that sufficient hydrogen is available for this reaction.²⁶ Since two distinct acetate hydrogenation products were observed in TPD for acetic acid on Pd(111), two sources of hydrogen were apparently available for this reaction. The acetic acid product desorbing with a maximum rate at 270 K most likely resulted from the reaction of adsorbed acetates with hydrogen atoms released to the surface by the initial dissociation of acetic acid. The scavenging of these hydrogen atoms by adsorbed acetates would diminish the concentration of hydrogen adatoms and delay the onset of H_2 desorption, consistent with experimental observations. The higher temperature acetate hydrogenation product was a consequence of the acetate decarboxylation reaction at 300 K. Hydrogen atoms generated by acetate decarboxylation reacted with the remainder of the acetate adlayer to produce acetic acid at 330 K. The hydrogenation of surface acetates to acetic acid occurred in parallel with the acetate decarboxylation reaction, and the relative rates of the two processes determined the reaction selectivity. At the maximum temperature for CO_2 desorption (300 K), the acetate decarboxylation pathway was dominant as evidenced by the minimum in the rate of acetic acid desorption at this temperature. The suppression of the acetate hydrogenation pathway between 260 and 300 K was due to the absence of hydrogen adatoms. However, as the acetate decarboxylation reaction proceeded and surface hydrogen was generated by this reaction, the rate of acetate hydrogenation increased at the expense of the decarboxylation pathway. Hydrogenation of C_1 hydrocarbons to methane appears to be sufficiently slow relative to that of acetate hydrogenation that no methane desorption was detected in TPD experiments. Instead, only decomposition was observed for the C_1 hydrocarbon fragments produced by acetate decarboxylation, resulting in the release of additional hydrogen atoms to the surface.

The CO_2 peak at 300 K in the acetic acid TPD spectrum clearly resulted from decomposition of surface acetates, as the reaction of adsorbed carbon monoxide with adsorbed oxygen atoms occurs between 400 and 500 K.²⁷

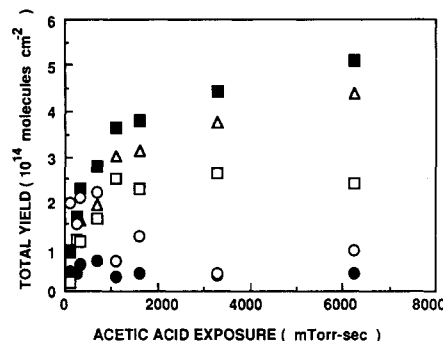


Figure 2. Product coverages determined from TPD following CH_3COOH adsorption at 170 K: (Δ) CH_3COOH ; (◻) CO_2 (×8); (●) CO; (○) H_2 ; (◼) total = $CH_3COOH + CO + CO_2$. The exposures are obtained by multiplying the dosing line pressure by the length of the exposure and provide only a relative measure of the flux to the surface.

The decomposition of acetic acid to CO must also liberate oxygen in some form. However, since no O_2 desorption was observed above 700 K, no CO_2 from CO oxidation was observed between 400 K and the desorption-limited evolution of CO at 490 K, and no oxidation of surface carbon was observed above 525 K,¹⁹ this oxygen must have been consumed by other reactions occurring at lower temperatures. The formation of H_2O is the obvious fate of the oxygen. The H_2O desorption spectrum following acetic acid adsorption at 170 K exhibited two peaks, one at 190 K and a very broad peak centered at 270 K. The 190 K peak is characteristic of the desorption of submonolayer quantities of molecular water from Pd^{26,28,29} and is located well above the 167 K peak observed by others for water ice.^{29,30} This small molecular H_2O peak (which represented less than 6% of the acetic acid coverage) may have been due to water impurities in the acetic acid or water adsorption from the chamber background. The broad peak at 270 K clearly represents a reaction product. This peak temperature is characteristic of the reaction of adsorbed hydrogen atoms and oxygen atoms on Pd(111).²⁶ Its width is somewhat broader than that observed when hydrogen and oxygen are coadsorbed; however, this observation is not surprising since the acetate decomposition reactions which release hydrogen and oxygen atoms to the surface span essentially the same temperature range of the TPD spectrum (250–350 K) as this H_2O peak. Thus there is a "feedback" from the acetate decomposition reaction which influences the hydrogenation/decomposition selectivity of adsorbed acetates. Hydrogenation and decomposition of acetates are in competition between 250 and 350 K; the decomposition of acetates to release CO also releases oxygen atoms which scavenge hydrogen atoms available for the competing hydrogenation pathway. This can be demonstrated further by preadsorption of oxygen atoms on the Pd(111) surface; their efficient scavenging of hydrogen completely suppresses the acetate hydrogenation channel observed at 270 K on the clean surface.²²

The effects of reducing the initial exposure of acetic acid below the saturation level are demonstrated by Figures 2 and 3. The total coverage increases rapidly at low exposure, reaching about 80% of its saturation value at

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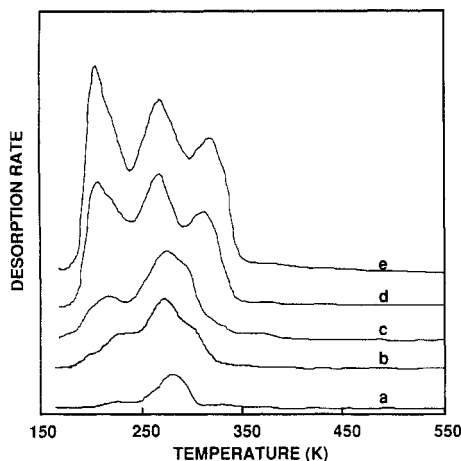


Figure 3. Variation of the CH_3COOH desorption spectrum with exposure equal to (a) 105 mTorr-s, (b) 240 mTorr-s, (c) 330 mTorr-s, (d) 1624 mTorr-s, (e) 6256 mTorr-s. See Figure 2 caption for explanation of exposure units.

ca. 20% of the saturation exposure. If one assumes an initial sticking probability of unity, the coverage required to saturate the surface at 170 K may be estimated to be 20 langmuirs. As shown in Figure 2, yields of CO and CO_2 level off at relatively low acetic acid exposures. A parallel trend was observed in the HREEL spectra discussed below: acetate species were of relatively greater importance for lower acetic acid exposures. The CO, H_2 , and H_2O (not shown) TPD yields at the lowest exposures exhibited the greatest scatter, most likely due to the relatively greater influence of adsorption of these background gases at low acetic acid coverages.

The variation with coverage of the desorption behavior of CH_3COOH is also consistent with the peak assignments above. As the initial coverage was reduced, the two peaks attributed to the reaction of adsorbed acetates with hydrogen atoms collapsed to a single peak at intermediate temperatures (285 K); the low-temperature (205 K) desorption peak for molecularly adsorbed acetic acid was strongly attenuated at low exposures. These observations again suggest that dissociative adsorption leading to decomposition in TPD is dominant at low coverages; molecular adsorption is favored at higher exposures.

HREELS experiments demonstrated that the adlayer produced by a saturation exposure of acetic acid on Pd(111) at 170 K was primarily molecular, although some evidence was found for dissociative adsorption to form surface acetate species. The HREEL spectrum for a saturation coverage of CH_3COOH on the clean Pd(111) surface at 170 K is shown in Figure 4, along with changes in the spectrum as the adlayer was annealed to progressively higher temperatures. The corresponding spectra for CH_3COOD and CD_3COOD are given in Figures 5 and 6, respectively. The presence of molecular acetic acid was indicated by the intense OH(OD) bending mode observed at 955 cm^{-1} for CH_3COOH , 700 cm^{-1} for CH_3COOD , and 695 cm^{-1} for CD_3COOD . Further evidence for the presence of molecular acetic acid was provided by the presence of the C=O stretching vibration at 1685 cm^{-1} and the C-O stretching mode at 1310 cm^{-1} in the spectrum recorded following CH_3COOH adsorption. Since both the $\nu(\text{C-O})$ and $\nu(\text{C=O})$ modes were dipole-active, the molecule must have been adsorbed such that the molecular plane was canted with respect to the Pd(111) surface normal. Although molecular acetic acid was the dominant surface species for saturation coverages of acetic acid at 170 K, the HREEL spectra also

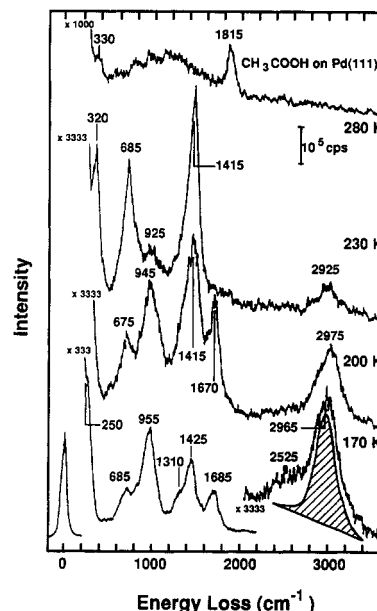


Figure 4. HREEL spectra for CH_3COOH adsorbed on Pd(111) at 170 K. Spectra denoted by higher temperatures were obtained after annealing to the indicated temperatures, following by cooling to 170 K. The shaded insert represents the C-H stretching region of ca. one-third monolayer of acetates produced by reaction of acetic acid at 170 K on the Pd(111)-(2 \times 2)O surface, followed by warming to 220 K.

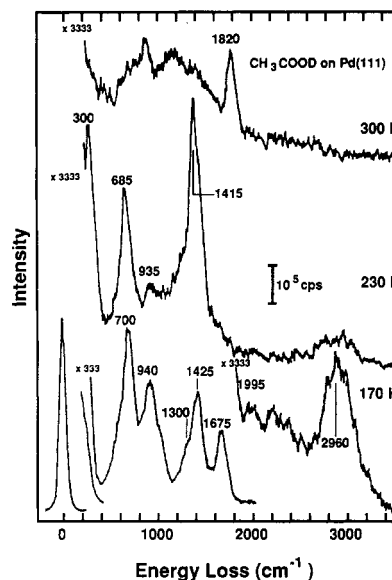


Figure 5. Temperature dependence of the HREEL spectra for CH_3COOD adsorbed on Pd(111).

indicated the presence of surface acetate species. Vibrations of adsorbed acetates were most clearly distinguished in the spectrum for CD_3COOD shown in Figure 6. For CD_3COOD adsorption on the Pd(111) surface, the vibration observed at 1410 cm^{-1} can be assigned solely to the symmetric OCO stretch of surface acetate species. In the spectra of both CH_3COOH and CH_3COOD , a strong loss was observed at 1425 cm^{-1} which consisted of the $\nu_s(\text{OCO})$ mode of acetate species and the $\delta(\text{CH}_3)$ modes of the acetic acid adlayer. There was no evidence for coadsorbates such as H_2O or OH in the HREEL spectrum at 170 K, as expected from the small amounts of H_2O evolved in TPD experiments. A summary of the vibrations of the adlayer produced by a saturation exposure of acetic acid on the clean Pd(111) surface is given in Table II, along with the vibrational frequencies observed

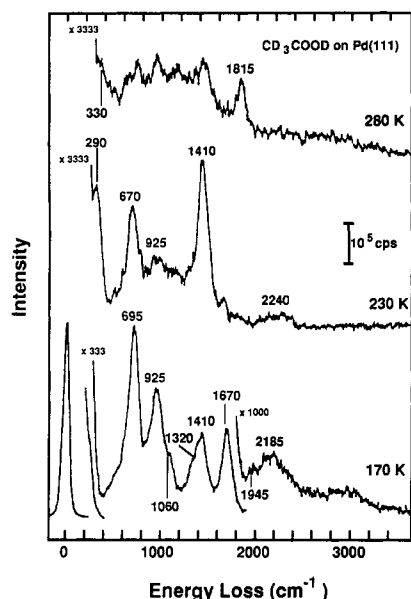


Figure 6. Temperature dependence of the HREEL spectra for CD_3COOD adsorbed on $\text{Pd}(111)$.

Table I. TPD Yields for Saturation Exposures of Acetic Acid on $\text{Pd}(111)$

product	T_p , K	yield, 10^{14} cm^{-2}
H_2O	190	0.3
CH_3COOH	205	1.2
CH_3COOH	270	1.6
H_2O	270	0.4
CO_2	300	0.3
CH_3COOH	330	1.6
H_2	375	0.9
CO	490	0.4
C(a)		0.4

Table II. Comparison of Vibrational Frequencies (cm^{-1}) of Acetic Acid Adsorbed on $\text{Pd}(111)$ and Acetic Acid with Varying Degrees of Hydrogen Bonding

mode	$\text{CH}_3\text{COOH(OD)}$	monomer ^a	dimer ^b	catemer ^c
$\nu(\text{CH}_3)$	2965	2997, 2961	3030	
$\nu(\text{OH})$	2525 (1995)	3577	3193	2875
$\nu(\text{C=O})$	1685	1799	1683	1648
$\delta(\text{CH}_3)$	1425	1401, 1340	1431, 1371	1448, 1356
$\nu(\text{C-O})$	1310	1279	1255	1284
$\gamma(\text{OH})$	955 (700)	1192	944	923
$\nu(\text{C-C})$	955	846	898	908
$\delta(\text{OCO})$	685	654	623	635
lattice	250			
$\nu_s(\text{OCO})$	1415 ^d			
-acetate				

^a Frequencies are for gaseous CH_3COOH from ref 12. ^b Frequencies are for liquid $(\text{CH}_3\text{COOH})_2$ from ref 12 and 13.

^c Frequencies are for crystalline $(\text{CH}_3\text{COOH})_n$ from ref 6.

^d Obtained after annealing to 230 K.

for the corresponding modes in IR studies of acetic acid monomers, dimers, and crystalline catemers.

The vibrational frequencies observed for the acetic acid adlayer at saturation coverage indicate a large degree of hydrogen bonding in the adlayer. Evidence for this hydrogen-bonding interaction was provided by the loss at 250 cm^{-1} in the spectrum for CH_3COOH at 170 K. Analogous vibrations have been observed for other adsorbates, such as H_2O , which display intermolecular hydrogen bonding.³¹ This vibration is due to the translation of hydrogen-bonded monomer units with respect to each other. Additional evidence for hydrogen bonding in the

acetic acid adlayer was provided by the frequency of the $\gamma(\text{OH})$ mode. Following the adsorption of CH_3COOH , the $\gamma(\text{OH})$ mode appeared at 955 cm^{-1} . This vibration was observed at 700 and 695 cm^{-1} in HREEL spectra recorded following the adsorption of CH_3COOD and CD_3COOD , respectively. In IR studies, this mode appeared at 923 cm^{-1} for crystalline CH_3COOH catemers,⁶ 944 cm^{-1} for liquid-phase CH_3COOH dimers,¹³ and 1192 cm^{-1} for gas-phase CH_3COOH monomers.¹¹ Although the large red-shift observed for the $\gamma(\text{OH})$ mode of CH_3COOH adsorbed on $\text{Pd}(111)$ clearly indicates the presence of a network of intermolecular hydrogen bonds, the extent of this hydrogen-bonding interaction could not be determined on the basis of this vibration alone.

Conclusive evidence for the formation of acetic acid catemers (i.e., $(\text{CH}_3\text{COOH})_n$) was supplied by the frequency of the $\nu(\text{OH})$ mode. A broad OH stretch was observed near 2525 cm^{-1} following CH_3COOH adsorption on $\text{Pd}(111)$. The large frequency shift observed for this mode (relative to the frequency of the $\nu(\text{OH})$ mode of gas-phase acetic acid) indicates the formation of acetic acid catemers on the $\text{Pd}(111)$ surface. In IR studies of crystalline $(\text{CH}_3\text{COOH})_n$, the OH stretching frequency was 2875 cm^{-1} .⁶ In contrast, gas-phase CH_3COOH monomers exhibit an OH stretching frequency of 3570 cm^{-1} .¹¹ Hubbard³² has also shown for pyridinecarboxylic acids bound to the $\text{Pt}(111)$ surface via the nitrogen function that free carboxyl groups which do not interact with the surface exhibit OH stretches around 3560 cm^{-1} . No evidence was found for vibrations in this region of the HREEL spectrum of the acetic acid adlayer, suggesting that isolated acetic acid molecules were not present on the $\text{Pd}(111)$ surface. The dosing conditions used in these experiments were chosen in order to ensure that the acetic acid dose admitted to the chamber contained a high concentration of monomers (at least 90%). The absence of a detectable amount of acetic acid monomers on the $\text{Pd}(111)$ surface under these conditions suggests that these species underwent rapid polymerization via intermolecular hydrogen bonding upon adsorption at 170 K. Since the hydrogen bonds in dimers are weaker than those in catemers, catemers are the more likely candidates for the hydrogen-bonded form of adsorbed carboxylic acids. On the basis of liquid-phase IR spectra, one would expect the $\nu(\text{OH})$ mode of acetic acid dimers to appear at 3190 cm^{-1} . Although there is no obvious peak in this region in Figure 4, the typical broadening of the loss peaks at higher frequency (e.g., in the C-H stretch region near 3000 cm^{-1}) could, in principle, obscure such a peak. In order to demonstrate that this was not the case, the envelope of the C-H stretching region for one-third monolayer of acetate species is shown by the shaded region of Figure 3. As noted above, adsorption of acetic acid on the clean $\text{Pd}(111)$ surface at 170 K produces one-third monolayer of molecules; reaction of acetic acid with preadsorbed oxygen atoms produces a pure layer of acetate species upon warming slightly to 220 K with approximately the same coverage of acetates on the oxygen-dosed surface as one obtains for acetic acid on the clean surface.^{21,22} Since there are no OH bonds in the acetate, the spectrum of this species provides an excellent fingerprint of the contribution of CH stretches to the vibrational spectrum of hydrogen-bonded acetic acid molecules. It is clear from comparison of the two spectra that they are essentially indistinguishable at frequencies greater

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than 2800 cm^{-1} but that the loss at 2525 cm^{-1} assigned to the $\nu(\text{OH})$ mode of acetic acid is quite prominent. The low frequency of this mode is consistent only with assignment to catemeric species, and the absence of a loss above 3000 cm^{-1} assignable to a $\nu(\text{OH})$ mode is clear evidence against the presence of dimers.

Since the frequency of the OH stretch of acetic acid catemers adsorbed on Pd(111) was $200\text{--}300\text{ cm}^{-1}$ lower still than that observed for crystalline acetic acid, coordination of acetic acid to the Pd(111) surface most likely occurred through the hydroxyl oxygen lone pair. Bonding of acetic acid to the surface in this manner would be expected to further weaken the OH bond, resulting in an additional reduction of the OH stretching frequency from the value observed for crystalline acetic acid catemers. In addition, coordination of acetic acid through the hydroxyl oxygen would permit the carbonyl oxygen atom to interact with neighboring hydroxyl hydrogens and would allow both the $\nu(\text{C-O})$ and $\nu(\text{C=O})$ modes of adsorbed acetic acid to be dipole-active. On the other hand, if coordination to the surface occurred through the carbonyl oxygen atom, the frequency of the $\nu(\text{C=O})$ mode would exhibit a small red-shift relative to that observed for acetic acid catemers, analogous to the frequency shift observed for the $\nu(\text{CO})$ mode of $\eta^1(\text{O})$ -coordinated aldehydes and ketones.^{19,23} The frequency of the C=O stretch of acetic acid catemers adsorbed on the Pd(111) surface was 1685 cm^{-1} , compared to 1648 cm^{-1} for crystalline acetic acid catemers. This observation indicates that there was no reduction in the C=O bond order due to coordination effects, consistent with coordination through the hydroxyl oxygen. Similarly, UPS studies of formic acid³³ and acetic acid³⁴ on Cu(110) have demonstrated that these adsorbates bind to this surface primarily through the oxygen non-bonding orbital localized on the hydroxyl group. Although this bonding mode is perhaps surprising, previous studies on Pd(111) in this laboratory have shown that the activation energies for desorption of alcohols (bound via the hydroxyl lone pair) and aldehydes bound via the carbonyl lone pair in a $\eta^1(\text{O})$ configuration are quite similar.^{18,19,26} The additional stabilization provided by hydrogen-bond formation may be decisive in determining which oxygen in the carboxylic acid interacts with the surface; this work and those noted above support an interaction at the hydroxyl oxygen.

The vibrations of molecular forms of acetic acid disappeared upon annealing the surface and were replaced by those of adsorbed acetate species. By 230 K, decomposition of the catemer species was complete, and HREELS experiments demonstrated that the adlayer consisted entirely of surface acetates. These acetates were characterized by intense vibrations at 1415 cm^{-1} ($\nu_s(\text{OCO})$), 685 cm^{-1} ($\delta(\text{OCO})$), and 320 cm^{-1} ($\nu(\text{Pd-O})$). Weaker losses at 1215 and 925 cm^{-1} were assigned to the $\delta(\text{CH}_3)$ and $\nu(\text{CC})$ vibrations, respectively. The vibrational frequencies of acetates adsorbed on Pd(111) were in agreement with IR studies of acetate salts.³⁵ The frequencies of these vibrations were also in agreement with those of acetate species produced by the adsorption of acetic acid on the oxygen-dosed Pd(111) surface.²² The absence of the $\nu_a(\text{OCO})$ vibration in the acetate vibrational spectrum (expected near 1580 cm^{-1}) indicates that these species must be adsorbed in a configuration with C_{2v} symmetry.

On the basis of the TPD results above, decomposition of acetic acid catemers resulted in the desorption of ace-

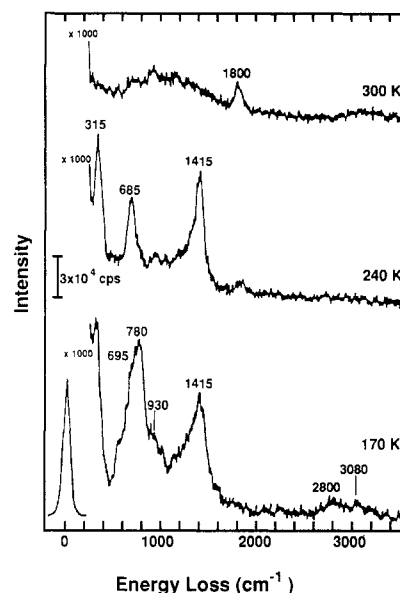


Figure 7. HREEL spectra for a subsaturation exposure of CH_3COOH on the Pd(111) surface. The total acetic acid coverage was estimated to be 1.5×10^{14} molecules cm^{-2} on the basis of TPD experiments at comparable exposures.

tic acid at 205 K. A substantial increase in the intensity of the acetate vibrations occurred upon annealing the adlayer to 220 K, suggesting that conversion to adsorbed acetate species also occurred during annealing. Between 220 and 260 K, only vibrations attributable to surface acetates were observed. However, upon annealing the surface to 280 K, a weak loss appeared at 1815 cm^{-1} signaling the presence of molecularly adsorbed CO. The appearance of this vibration coincided with the acetate decomposition observed in TPD experiments. The intensity of the $\nu(\text{CO})$ mode of CO(a) reached a maximum value after annealing to 300 K and did not change significantly for temperatures up to 450 K. The observation of this product in HREELS experiments is consistent with the observation in TPD experiments that acetate decomposition occurred via competitive reactions to form CO and CO_2 on Pd(111). Similar reactions have been observed for acetate decomposition on the Ni(111) surface.¹⁷ In addition, after annealing to 280 K a broad peak emerged near 1100 cm^{-1} . While the broad nature of this peak precluded an exact assignment, this loss was most likely due to the vibrations of surface methylene and methylidyne species produced by acetate decomposition. As discussed previously,¹⁹ methylene species adsorbed on the Pd(111) surface are characterized by losses at 1430 and 935 cm^{-1} , assigned to the $\delta(\text{CH}_2)$ and $\rho(\text{CH}_2)$ modes, respectively.

Experiments were also conducted to determine the effect of acetic acid coverage upon the HREEL spectrum. Figure 7 shows the HREEL spectra at 170, 240, and 300 K following the adsorption of a subsaturation exposure of CH_3COOH on the Pd(111) surface. The acetic acid coverage used in these HREELS experiments was approximately one-tenth monolayer (i.e., 30% of the saturation coverage). At 170 K, vibrations of adsorbed acetate species were clearly dominant, as evidenced by the relatively intense loss at 1415 cm^{-1} ($\nu_s(\text{OCO})$) and the much weaker $\gamma(\text{OH})$ vibration than observed at saturation coverage. However, peaks suggestive of incomplete dissociation were also observed between the characteristic acetate peaks at 685 and 1415 cm^{-1} . Upon annealing the surface to 240 K, the intensities of acetate vibrations increased, and no evidence could be found for adsorbed

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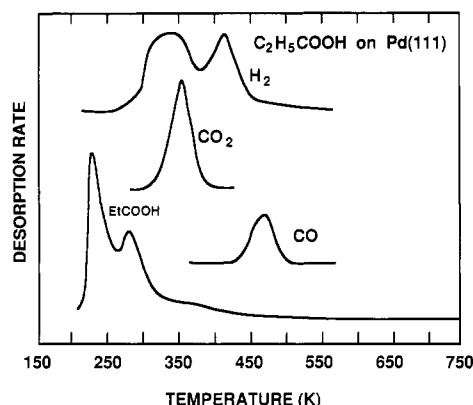


Figure 8. TPD spectrum for the reaction of propanoic acid on the clean Pd(111) surface.

acetic acid. Annealing the surface to 300 K resulted in the complete disappearance of the vibrations of adsorbed acetate species and the appearance of vibrations of CO(a) and adsorbed C_1 hydrocarbons. These results indicate that the adsorption of acetic acid on the clean Pd(111) surface was largely dissociative at low coverages but that molecular adsorption became increasingly more important as the surface concentration of acetic acid increased.

The influence of the dosing line pressure upon the reactivity of acetic acid on the Pd(111) surface was also examined. On the Ni(111) surface, Schoofs and Benziger¹⁷ observed that increasing the concentration of acetic acid dimers in the dosing line altered the selectivity of acetate decomposition reactions. One method for increasing the dimer concentration in the dosing line is to raise the dosing line pressure. HREEL spectra presented in Figures 3–5 were recorded for acetic acid adsorption with a dosing line pressure of 100 mTorr at 298 K, which is similar to that used by Schoofs and Benziger for monomer adsorption.¹⁷ The dimer concentration in the dosing line under these conditions was calculated to be roughly 10%. Acetic acid was also dosed onto the clean Pd(111) surface with a dosing line pressure of 1000 mTorr at 298 K (dimer concentration roughly 45%). The dosing conditions used by Schoofs and Benziger for dimer formation were 200 mTorr at 238 K.¹⁷ In our experiments, the HREEL spectra recorded for the higher line pressures of acetic acid were identical with those shown in Figures 4–6, indicating that an enhancement of the gas-phase concentration of the carboxylic acid dimers in the dosing line did not produce an increase in concentration of acetic acid dimers on the surface. This observation can be explained by the dissociation of carboxylic acid dimers to adsorbed monomers upon adsorption on the Pd(111) surface at 170 K.

Propanoic Acid. The reaction pathways observed for propanoic acid on the clean Pd(111) surface were analogous to those of acetic acid. TPD experiments shown in Figure 8 indicated that adsorbed propanoic acid either desorbed at 230 K or dissociated to surface propanoate species. A portion of these propanoates reacted via hydrogenation to propanoic acid at 280 K; some activity for propanoate decomposition at 355 K was also observed. Propanoate decomposition resulted in the desorption of CO_2 and propanoic acid at 355 K and the release of C_2 hydrocarbon species to the surface. Decomposition of these C_2 hydrocarbons occurred at 415 K, resulting in the desorption of reaction-limited H_2 at this temperature and the formation of a carbon adlayer. On the basis of the product yields given in Table III, only 50% of the propanoates formed by propanoic acid dissociation on

Table III. Product Yields for Propanoic Acid TPD

product	peak temp, K	yield, 10^{14} cm^{-2}
CH_3CH_2COOH	230	1.1
CH_3CH_2COOH	280	0.6
H_2	340	0.8
CO_2	355	0.4
CH_3CH_2COOH	355	0.2
H_2	415	0.4
CO	470	0.4
C(a)		0.3

Pd(111) underwent hydrogenation to propanoic acid at 280 K, even though hydrogen adatoms were in excess as evidenced by the large amount of H_2 evolved at 340 K. In contrast, over 90% of the acetate species produced by the dissociation of acetic acid on Pd(111) underwent hydrogenation to acetic acid between 250 and 340 K. These observations suggest that surface propanoates exhibited a lower tendency for hydrogenation reactions on Pd(111) than did acetate species.

The desorption of H_2 occurred in two peaks at 340 and 415 K following adsorption of propanoic acid on Pd(111). The lower temperature H_2 product was identified as desorption-limited H_2 by comparison with the peak shape and desorption temperature of H_2 following the dissociative adsorption of dihydrogen.²⁴ Hydrogen desorbed at 340 K, even though propanoate species were present on the surface at this temperature as indicated by their subsequent decarboxylation at 355 K. Thus, the recombination of hydrogen adatoms to form $H_2(g)$ becomes competitive with the propanoate hydrogenation reaction for temperatures above 260 K. The H_2 product desorbing at 415 K resulted from the decomposition of C_2 hydrocarbon species generated by the propanoate decomposition reaction. While the identity of this C_2 hydrocarbon cannot be determined from the TPD data alone, this species could not have been ethynyl (CCH_3), as the H_2 desorption temperature was ca. 40 K lower than that for H_2 produced by ethynyl decomposition on Pd(111).^{18,36}

HREEL spectra for the reaction of propanoic acid on Pd(111) indicated the presence of both molecular propanoic acid and surface propanoate species at 170 K. Further, a large degree of intermolecular hydrogen bonding was present in the adlayer as evidenced by the large red shift of the OH stretching frequency from that observed for gas-phase propanoic acid. The HREEL spectra recorded following propanoic acid adsorption on Pd(111) are given in Figure 9 as a function of the temperature to which the adlayer was annealed. Assignment of the observed vibrational modes of the adlayer was analogous to that discussed above for acetic acid and is summarized in Table IV along with the vibrational frequencies of propanoic acid dimers.

Several significant differences were observed between the vibrational spectra of propanoic acid adsorbed on Pd(111) and of propanoic acid dimers. The OH stretching frequency of the adlayer produced by propanoic acid adsorption on Pd(111) was 2555 cm^{-1} . The frequency of this mode was similar to that observed for the corresponding vibration of acetic acid on Pd(111) and indicates the presence of strong intermolecular hydrogen bonds, as expected with catemer formation. In contrast, the weaker hydrogen-bonding interaction observed for crystalline propanoic acid dimers was characterized by a $\nu(OH)$ mode near 3000 cm^{-1} .¹⁴ As demonstrated for acetic acid, com-

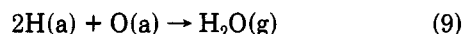
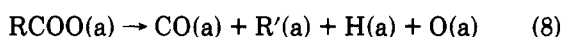
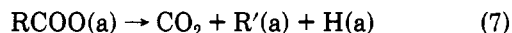
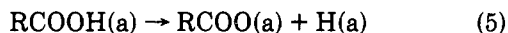
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by dehydrogenation of the ethyl species presumably produced by propanoate decarboxylation; a similar conclusion may be drawn from data for ethylidyne formation via decarbonylation of acrolein and propanal on Pd(111).²³

Discussion

Carboxylic acids adsorbed on the Pd(111) surface exhibited a complex chemistry with a number of factors controlling the reaction selectivity. Carboxylic acid monomers were initially adsorbed through the hydroxyl oxygen and underwent rapid polymerization via intermolecular hydrogen bonding at 170 K to produce catemers. Both formic acid and acrylic acid exhibit similar behavior on Pd(111).^{21,22} On the clean Pd(111) surface, both acetic acid and propanoic acid exhibited a tendency for molecular desorption between 190 and 230 K. In addition to this desorption pathway, dissociation of carboxylic acid catemers produced surface carboxylates. Carboxylate decomposition occurred primarily via decarboxylation on clean Pd(111) and resulted in the desorption of CO₂ and the release of hydrocarbons and/or hydrogen to the surface.

The reaction of carboxylic acids on the Pd(111) surface involved several competitive reaction channels, with the relative importance of each pathway dependent upon a number of variables. Carboxylic acid reactions on Pd(111) appear to occur via the sequence



where R represents the substituent on the carboxyl group. The temperatures at which these reactions occurred varied widely for the carboxylic acids studied. For example, catemer decomposition (step 3) occurred at 205 K for acetic acid and 230 K for propanoic acid. The temperature at which CO₂ evolution from carboxylate decomposition reactions was observed also varied for the carboxylic acids. CO₂ was evolved from formate at 260 K,²¹ from acetates at 300 K, and from propanoates at 355 K. The details of the decomposition of carboxylate species will be discussed further in a future publication.²²

The behavior of acetic acid on Pd(111) demonstrates the effect of carboxylic acid concentration upon the reaction selectivity. Following a saturation exposure of acetic acid, catemer formation (step 2) was dominant, while this pathway was less important at low acetic acid coverages. In addition, the relative importance of the carboxylate hydrogenation and decarboxylation pathways depended upon coverage, as shown in Figure 2. The production of CO and CO₂ from decomposition of surface acetates reached a plateau at lower coverages than did any of the acetic acid desorption peaks. The relative rates of carboxylate hydrogenation and decomposition reactions and of competing hydrogen-scavenging reactions of surface oxygen released by decomposition control the reaction selectivity. Following the adsorption of acetic acid

on Pd(111), acetate hydrogenation to acetic acid first occurred at 270 K. This reaction consumed most of the hydrogen present at this temperature, resulting in a drop in the rate of acetic acid desorption between 270 and 300 K. Acetate decomposition (steps 7 and 8) as fingerprinted by CO₂ desorption reached a maximum at 300 K, releasing additional hydrogen atoms to the surface. The hydrogen adatoms generated by this reaction consumed the remainder of the acetate adlayer to produce acetic acid at 330 K. The rate of acetate hydrogenation apparently overtook that of acetate decarboxylation at 300 K. Thus, hydrogenation became dominant for temperatures greater than 300 K, at the expense of the acetate decarboxylation reaction.

One of the factors influencing the selectivity of carboxylic acid reactions on metal surfaces appears to be the degree of hydrogen bonding present in the adlayer. Benziger and Schoofs reported strikingly different selectivities for the reactions of monomers and dimers of formic acid¹⁶ and acetic acid¹⁷ on Ni(111) surfaces. Both monomers and dimers were adsorbed from the gas phase, and no evidence was found by these investigators for the formation of dimers by association of monomer units once these species were adsorbed on the Ni(111) surface. In the present experiments, no evidence was found in either TPD or HREELS for the presence of carboxylic acid dimers adsorbed from the gas phase, and stable carboxylic acid monomers were not observed on the Pd(111) surface under any conditions. However, recent HREELS studies of formic acid adsorbed on the Pd(100) surface can be interpreted as suggesting the presence of both molecular formic acid ($\nu(\text{OH}) = 3320 \text{ cm}^{-1}$) and formic acid catemers ($\nu(\text{OH}) = 2660 \text{ cm}^{-1}$) at 80 K.⁵¹ Thus, formic acid monomers appear to be stable on metal surfaces only at low temperatures. The absence of detectable amounts of carboxylic acid dimers on the Pd(111) surface is consistent with the weak hydrogen-bonding interaction in these species. The hydrogen bond of carboxylic acid catemers is stronger by several kcal/mol than that of carboxylic acid dimers.¹⁵ Since catemer decomposition occurred near 200 K on the Pd(111) surface, the decomposition of dimer species adsorbed from the gas phase would be expected to occur at lower temperatures. Thus, if carboxylic acid dimers were adsorbed from the gas phase, they would be expected to decompose to carboxylic acid monomers. These monomers would then undergo rapid polymerization at 170 K via hydrogen-bonding interactions to form the carboxylic acid catemers observed by HREELS.

HREELS experiments suggest that aliphatic carboxylic acids adsorb on the Pd(111) surface through the oxygen lone pair of the hydroxyl oxygen. Interactions between neighboring carboxylic acid monomers lead to hydrogen-bond formation involving the hydroxyl hydrogen of one monomer and the carbonyl oxygen of a second monomer. This hydrogen-bonding interaction propagates through the adlayer resulting in the formation of catemers. The observation of hydrogen-bonded catemers following adsorption of formic acid²¹ or acetic acid on Pd(111) is not surprising, since thermodynamics favors the crystallization of these molecules as catemers and since formation of crystalline catemers by vapor-phase deposition at 77 K has also been reported.^{1,2} Further, vibrations attributable to the $\nu(\text{OH})$ mode of hydrogen-bonded catemers have been reported previously in HREELS studies of formic acid adsorbed on Pd(100),⁵¹

Pt(111),⁵² and Ag(110)⁵³ surfaces. Evidence for hydrogen-bond formation was also obtained in UPS studies of formic acid adsorbed on thin films of Cu, Ni, and Ag, although the low resolution of these experiments did not permit a determination of the nature of the hydrogen-bonding interaction.⁵⁴

Other molecules such as water and methanol undergo intermolecular hydrogen bonding when adsorbed on metal surfaces. However, the strength of the hydrogen-bonding interaction for these adsorbates is lower than that observed in carboxylic acid adlayers. For example, water forms a relatively weak hydrogen bond on most metal surfaces, and the frequency of the $\nu(\text{OH})$ mode varies between 3230 cm^{-1} (for O/Ag(110)) and 3460 cm^{-1} (for Pd(100)).³¹ In contrast, the $\nu(\text{OH})$ mode of solid H_2O occurs at 3220 cm^{-1} .³¹ The increase in the frequency of the $\nu(\text{OH})$ mode of H_2O adsorbed on metal surfaces (relative to that observed for bulk H_2O) reflects the extent to which the surface perturbs the crystal structure of H_2O relative to that of bulk H_2O and weakens the hydrogen bond. Alcohols adsorbed on the clean Pd(111) surface also exhibit a relatively weak hydrogen bond. For example, the frequency of the $\nu(\text{OH})$ mode of monolayer coverages of methanol on Pd(111) is 3355 cm^{-1} .⁵⁵ The $\nu(\text{OH})$ mode of crystalline methanol appears at 3275 cm^{-1} .⁵⁶

The presence of propanoic acid catemers following adsorption of propanoic acid on the clean Pd(111) surface provides insights into the polymerization of carboxylic acids on metal surfaces. Crystallization of carboxylic acids is controlled by steric factors arising from the three-dimensional packing of the monomer units. These steric factors are sensitive to the size of the alkyl substituent on the carboxyl group and may render catemerization less favored and dimerization more favored thermodynamically, depending upon their extent.⁷⁻⁹ Thus, steric repulsion between ethyl substituents of neighboring propanoic acid molecules promotes the crystallization of this species in the dimer motif, as established by IR⁴ and crystallographic studies¹⁰ of solid propanoic acid. While the three-dimensional packing of carboxylic acid polymers is important in the crystalline phase, polymerization of carboxylic acids on metal surfaces involves packing of the polymer in only one or two dimensions. For one- and/or two-dimensional packing, steric interactions arising from the presence of the relatively large alkyl substituent of propanoic acid would be less important than for three-dimensional packing. This difference could account for the formation of catemers from propanoic acid adsorbed on the Pd(111) surface, analogous to the behavior observed for acetic acid on Pd(111). Dimerization of adsorbed monomer units of propanoic acid is less likely due to the binding of these molecules to the Pd(111) surface. Thus, for adsorption of monolayer quantities of propanoic acid on the Pd(111) surface, the thermodynamics of hydrogen bonding shifts from favoring dimer formation (as observed for crystalline propanoic acid) to favoring catemer formation. However, if multilayers of propanoic acid were condensed on the Pd(111) surface, three-dimensional packing effects would become important in the multilayer region, and dimer formation would be expected to occur.

The alkyl substituents of these carboxylic acids had a dramatic influence on their reactivities. Although formic acid, acetic acid, and propanoic acid decomposed via carboxylate species, different thermal stabilities were observed for the carboxylates derived from these acids. Formate species were the least stable on the Pd(111) surface and decomposed at 260 K.²¹ The stability of acetate species was slightly greater than that of formates, as acetate decomposition occurred at 300 K. Propanoate species produced by the dissociation of propanoic acid on the Pd(111) surface exhibited the greatest thermal stability among the aliphatic carboxylates studied. Propanoate decomposition occurred at 350 K. Thus, on the clean Pd(111) surface, the stability of carboxylates increases with increasing chain length.

Additional insights into the influence of the substituents on hydrogen-bonding interactions can be gained by a comparison of the results of this study with previous studies of Langmuir-Blodgett films of large carboxylic acids. Langmuir-Blodgett films of several fatty acids have been studied by HREELS on polycrystalline Ag^{57,58} and by FTIR-ATS on Ge.⁵⁹ These works examined fatty acids with a minimum of 17 carbon atoms in the alkyl substituent (e.g., $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$). FTIR-ATS studies on Ge suggest that these carboxylic acids are adsorbed through the hydroxyl oxygen at monolayer coverages, with the carboxyl $\text{C}=\text{O}$ bond roughly parallel to the surface due to lateral interactions between alkyl substituents on neighboring carboxyl groups.⁵⁹ Orientation of the adsorbed fatty acids in this manner appears to suppress hydrogen-bond formation at monolayer coverages. However, at multilayer coverages, vibrational data indicate significant hydrogen bonding in the multilayer, resulting in the formation of dimers, consistent with the behavior of crystalline fatty acids.⁵⁹ Similar observations could not be made in HREELS experiments on polycrystalline silver because of the lower resolution of these experiments.^{57,58} Although carboxylic acids are also adsorbed through the hydroxyl oxygen on the Pd(111) surface, the $\text{C}=\text{O}$ bond of the carboxyl group was not oriented parallel to the surface, as both the $\nu(\text{C}-\text{O})$ and $\nu(\text{C}=\text{O})$ modes were dipole-active in HREELS. Further, more extensive hydrogen bonding was observed in adlayers of acetic acid and propanoic acid on Pd(111) than observed for Langmuir-Blodgett films. Thus, the smaller substituents of these carboxylic acids permit a greater hydrogen-bonding interaction between neighboring molecules (presumably due to the proximity of hydroxyl hydrogens and carboxyl oxygen atoms) than observed for fatty acid monolayers prepared by Langmuir-Blodgett methods.

Conclusions

On the clean Pd(111) surface, carboxylic acids are adsorbed as monomers through the hydroxyl oxygen lone-pair orbital. Interactions between neighboring molecules lead to hydrogen-bond formation, which propagates through the adlayer to produce carboxylic acid catemers at 170 K. The stability of these catemers was dependent upon the identity of the adsorbed acid. Acetic acid catemers decomposed at 200 K, while catemer species produced by the adsorption of propanoic acid decomposed at 230 K. The reaction of carboxylic acids

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on the Pd(111) surface resulted in the formation of surface carboxylates which either decomposed via decarboxylation or underwent hydrogenation to the corresponding carboxylic acid.

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Effects of Presulfidization on the Selectivity and Surface Structure of Ruthenium Catalysts[†]

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X-ray photoelectron spectroscopy and static secondary ion mass spectrometry have been used to reveal details about the adsorption sites and surface phases which are formed on ruthenium catalysts following pretreatment in H₂-rich or H₂S-rich sulfidization mixtures. While sulfidization in as little as 29 ppm H₂S/H₂ at 673 K can be used to produce the bulk sulfide, RuS₂, the surface instability of S⁻-S⁻ anion pairs, found in the pyrite-RuS₂ lattice, requires that ≥80% H₂S/H₂ be used at 673 K before these species are stabilized at the surface. Co-adsorption of H₂-D₂ mixtures on extensively sulfided catalysts, followed by static SIMS analysis, reveals mixtures of S₂H₂⁻ and S₂D₂⁻ with little or no S₂HD⁻ being detected. Isolated anion pairs are thereby identified as active sites for irreversible hydrogen adsorption and presumably the unique selectivity patterns which sulfided ruthenium catalysts possess following sulfidization in H₂S-rich mixtures. Little or no irreversible hydrogen adsorption is measured over metallic ruthenium surfaces retaining ≥0.25 monolayer of strongly bound sulfur or over bulk RuS₂ materials sulfided in <80% H₂S/H₂ at 673 K.

Introduction

Kinetic and selectivity studies of thiophene hydrodesulfurization (HDS) over sulfided ruthenium catalysts have revealed two different selectivity regimes depending on the presulfidization conditions employed.^{1,2} Presulfidization in hydrogen-rich mixtures (e.g., 101 kPa, 10% H₂S/H₂) at temperatures from 298 to 1073 K produces a catalytic surface which yields only the direct hydrogenolysis products of C₄ hydrocarbons and H₂S (i.e., the type A surface). On the other hand, presulfidization in hydrogen sulfide rich mixtures (e.g., 101 kPa ≥80% H₂S/H₂) at temperatures greater than 673 K produces a catalytic surface which yields high levels of hydrogenation products including tetrahydrothiophene (i.e., the type B surface). While the full origin of the above noted difference in catalytic selectivity has not been directly demonstrated by analytical means, characterization efforts have proved helpful in identifying property-specific attributes and distinctions which exist between the two surfaces. These pieces of information have been combined and used to develop/infer a phenomenological picture for the structure of each surface.

The most revealing aspect/trend which has arisen from various characterization efforts and tandem kinetic stud-

ies is the reversible nature of the transition which occurs between the two selectivity regimes. The well-defined and rather narrow H₂S/H₂ concentration ratio over which this transition occurs is suggestive of a phase change. Pulse oxygen chemisorption data, hydrogen adsorption studies, and H₂-D₂ equilibration results all provide reversible trends within the same H₂S/H₂ temperature envelope.¹⁻³ Microgravimetry and XRD analyses further suggest that this transition is confined to the surface, as only about one monolayer equivalent of sulfur addition is involved in going from the type A to the type B surface, and no changes in bulk structure are observed.² Measurements of the H₂S/H₂ ratio and temperature required to promote the selectivity transition have also been used to estimate a free energy of ca. +7 kJ/mol required to form the high hydrogenation (i.e., type B) surface² as compared to the value of -59 kJ/mol required to form RuS₂ in the bulk (viz., Ru⁰ + 29 ppm H₂S/H₂ = RuS₂ + H₂, at 673 K).

While the free energy required for the surface-phase transformation can be readily estimated, the corresponding structure of each surface is still in question. Hydrogen adsorption studies³ and vibrational studies of adsorbed hydrogen using inelastic incoherent neutron scattering (IINS)⁴ show that hydrogen is retained on the type B surface as sulfhydryl groups, while little or no hydrogen is bound in a reversible or irreversible fashion to the type A surface. On the basis of these results and additional studies of thiophene adsorption on sulfur-preadsorbed

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