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MBRS Measurements of Overlayer Effects on Surface Lifetimes and Reaction Probabilities

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The interaction of formic acid with Ni(110), Ni(110)–carbide, Ni(110)–graphite, and Ni(110)–sulfide surfaces was examined by molecular beam relaxation spectrometry. The apparent first-order rate constants for the desorption of formic acid ($T_s < 300°K$) were remarkably similar on all of the surfaces studied, suggesting that the low-temperature formic acid adsorption/desorption interactions were essentially identical on the different catalytic surfaces investigated. The onset of formic acid decomposition occurred in the vicinity of room temperature for the different surfaces examined, and the decomposition probabilities above room temperature varied appreciably from surface to surface. The decomposition probabilities above room temperature were 0.9 for Ni(110), 0.5 for Ni(110)–carbide, and <0.1 for Ni(110)–graphite and Ni(110)–sulfide.

I. INTRODUCTION

The flash desorption of formic acid was shown to exhibit different behavior on the Ni(110), Ni(110)–carbide, and Ni(110)–graphite surfaces subsequent to low temperature adsorption (*1–5*). Formic acid desorbed from the Ni(110) surface (*5*) by a first-order process with a coverage-dependent activation energy, desorbing in a single peak below room temperature. As the formic acid exposure was increased, the peak temperature decreased from 263 to 237°K. The desorption rate curve on the carbide surface peaked at 213 ± °K (*3*), indicating a weaker interaction with the surface. On both the Ni(110) and Ni(110)–carbide HCOOH desorbed from surfaces covered with a monolayer of chemisorbed formic acid in the form of formate or formic anhydride (*3, 5*). These surface intermediates were stable until higher temperatures and decomposed above room temperature. Furthermore, the initial desorption rate from the graphitic overlayer (*3*) showed zero-order desorption kinetics, and this behavior was attributed to the formation of a hydrogen bonded condensed phase on the graphite surface. The present investigation was undertaken to investigate the interaction of gas phase HCOOH with these substrates.

In the present study the surface lifetimes and reaction probabilities of formic acid on Ni(110) and Ni(110) with chemilayers of carbide, graphite, and sulfur were examined over a wide temperature range with MBRS. The interaction of formic acid with the (110) oriented nickel surface was extensively investigated by MBRS and has been discussed elsewhere (*6*). The results obtained with the molecular beam of HCOOH are compared below with the HCOOH flash desorption results previously reported.

II. EXPERIMENTAL

The ultrahigh vacuum molecular beam relaxation spectrometry (MBRS) system utilized in this study was previously described (*1, 6*). The UHV chamber was equipped with a modulated molecular beam system, PHI four-grid LEED-Auger optics, an argon ion bombardment gun, and a UTI 100C quadrupole mass spectrometer. The base pressure of the UHV system was usually about 2×10^{-10} Torr and increased to the low 10^{-9} Torr range when the molec-

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ular beam was operating. The flux of the HCOOH molecular beam at the Ni(110) surface was kept constant throughout the experiment at approximately 10^{13} molecules/cm^2 sec. The molecular beam of formic acid was generated by an array of fused capillaries of 0.005 cm diameter and subsequently collimated by a 2-mm hole that separated the beam source from the main chamber. The beam was then modulated inside the main chamber; modulation frequencies of 20–150 Hz were readily attainable. The surface normal of the crystal was held at aproximately 45° from both the beam axis and the mass spectrometer. The ac signal from the mass spectrometer was examined with both an Ithaco Dynatrac 391A phase-sensitive lock-in detector and a PAR TDH-9 waveform eductor. Desorbing formic acid was detected by monitoring the 29AMU, HCO^+, fragment. Since the ac signal-to-noise ratio was large, it was only necessary to use a 1.25-sec time constant for the phase-sensitive detector. The waveforms were just examined on an oscilloscope and then plotted on an X-Y recorder. Typical time constants used in storing the product response curves ranged from 20 to 50 sec. The signals were extremely reproducible from experiment to experiment because of the large signal-to-noise ratio. The transit time of the system was determined by measuring the phase-lag for a molecular beam of argon.

The single-crystal sample (0.5 × 1.0 × 0.005 cm) was cooled by thermal contact with a liquid nitrogen reservoir to temperatures approaching 165°K. The sample temperature was measured by a chromel-alumel thermocouple spot welded to the edge of the Ni(110) sample. The sample was heated from a tungsten filament located behind the crystal face. The procedures for preparing the different surface chemilayers are described below.

The surfaces were examined at the beginning and end of each experiment with Auger electron spectroscopy (AES) and were found to be stable to prolonged formic acid exposure at the pressures and temperatures employed in this investigation. The carbide and graphite overlayers were formed by exposing a clean Ni(110) surface to ethylene at 610 and 780°K, respectively (*2*). The sulfur overlayer was obtained by heating the sample and allowing bulk sulfur to segregate to the nickel surface. Unfortunately this procedure also yielded a substantial carbon Auger peak. The surface prepared in this manner consisted of a monolayer of approximately 75% sulfur and the rest carbon. A carbon monolayer was defined as the saturation carbon coverage obtained from cracking ethylene to saturation coverage on the nickel surface. A coverage of 1.1×10^{15} sulfur atoms/cm^2 was defined as a surface monolayer; the AES sensitivities for the sulfur and nickel peaks were estimated to within a factor of two (*7*).

III. RESULTS

Formic acid reaction products (i.e., CO_2, CO, H_2, and H_2O) were not produced below room temperature on the various surfaces, and the only process observed was the adsorption and desorption of formic acid from the different substrates. The waveforms for the desorption of formic acid from the Ni(110)–graphite surface below room temperature are presented in Fig. 1. The low temperature waveforms showed no evidence of reflected components at the specular angle, since reflected molecules would appear as a sharp step in the HCOOH signal at time zero. The discontinuity would occur because a portion of the incident molecules would be instantaneously reflected, while the remaining molecules would undergo a first-order process and, as a result, desorb exponentially (*6*). Although the waveforms presented are only for the Ni(110)–graphite surface, similar waveforms were also obtained for the other surfaces. It was concluded from this observation that the adsorption probability of formic acid was essentially unity for all of the surfaces investigated, and that the in-

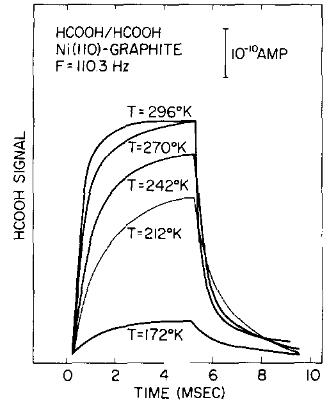

FIG. 1. Smoothed waveforms for the desorption of formic acid from the Ni(110)–graphite surface below room temperature.

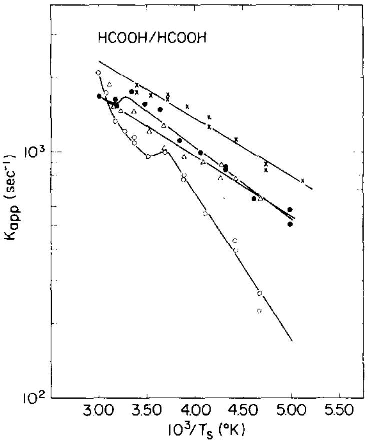

FIG. 2. The apparent first-order rate constants for the desorption of formic acid molecules from (○) Ni(110); (●) Ni(110)–carbide; (×) Ni(110)–graphite: (△) Ni(110)–S + C.

coming beam of HCOOH completely desorbed at the end of the cycle.

The apparent first-order rate constants for the desorption of formic acid were directly calculated from the lock-in phase-lag utilizing the relationship (*6*).

$$k_{\text{app}} = \frac{\omega}{\tan\phi} \qquad (1)$$

where ϕ was the measured phase-lag, and ω was the modulation frequency in radians/sec ($\omega = 2\pi f$); the rate constants were also calculated from the exponential decay of the waveforms (*6*). Both methods gave precise agreement. The apparent first-order rate constants for formic acid desorption from the different surfaces (T_s < 300°K) are presented in an Arrhenius fashion in Fig. 2. The desorption rate constants were calculated to be:

$$k_{\text{nickel}} = 1.6 \times 10^5 \exp[-2.73 \text{ kcal/mole}/RT] \text{ sec}^{-1} \qquad (2)$$

$$k_{\text{carbide}} = 1.5 \times 10^4 \exp[-1.31 \text{ kcal/mole}/RT] \text{ sec}^{-1} \qquad (3)$$

$$k_{\text{graphite}} = 1.2 \times 10^4 \exp[-1.06 \text{ kcal/mole}/RT] \text{ sec}^{-1} \qquad (4)$$

$$k_{\text{sulfur}} = 8.9 \times 10^3 \exp[-1.11 \text{ kcal/mole}/RT \text{ sec}^{-1} \qquad (5)$$

The activation energies and preexponential factors for formic acid desorption were very similar for the series of surfaces examined. Note that for the Ni(110) and Ni(110)–carbide surfaces the Arrhenius plots were linear at low temperatures, but the apparent rate constants for desorption decreased at the highest temperatures studied below that expected from the adsorption–desorption behavior extrapolated from lower temperatures. This behavior was due to the onset of a new reaction channel: the decomposition of formic acid. For a more detailed discussion of this phenomenon refer to Wachs and Madix (*6*). It is also important to note that AES analysis of the Ni(110) sample showed surface oxygen and carbon were present subsequent to HCOOH exposure (*6*).

The lock-in ac amplitudes for the formic acid molecules desorbing from the different surfaces are presented in Fig. 3 for the range of temperatures investigated. Below room temperature all the amplitudes behaved in a similar fashion and decreased with decreasing surface temperature due to

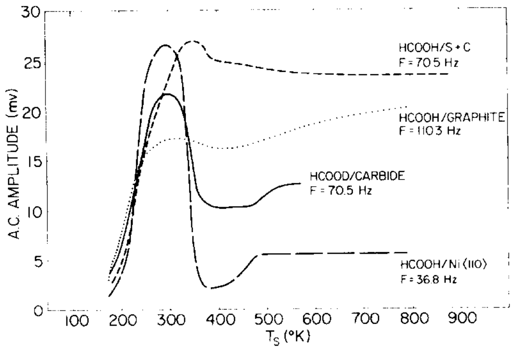

FIG. 3. Amplitudes of the lock-in detector signals for the desorption of formic acid from the different surfaces investigated versus surface temperature.

the influence of frequency demodulation. The onset of formic acid decomposition occurred in the vicinity of room temperature on all the surfaces, but the extent of decomposition above room temperature was different for each surface. The decomposition probability was calculated from the amplitude attenuation above room temperature and was plotted in Fig. 4 as a function of temperature. The Ni(110) surface was the most active toward the decomposition of HCOOH and exhibited a decomposition probability greater than 0.9 at 375°K which decreased to 0.8 at higher surface temperatures even though this surface showed appreciable carbon and oxygen coverage! The formation of surface carbide from the formic acid decomposition products was probably responsible for the slight decrease in the decomposition probability above 400°K (*6*). The decomposition probability of formic acid on the carbide overlayer was 0.50 above 375°K, and the reactivity of this surface was intermediate between the Ni(110) and the graphite and sulfur overlayers. The formic acid signal on the graphite overlayer decreased slightly above 300°K and increased again above 400°K; the decrease was due to decomposition, and the increase in the formic acid ac signal at higher temperatures was the result of the strong demodulation effect of the high frequency utilized (110 Hz). The graphite and sulfur overlayers exhibited very little reactivity ($P < 0.1$) below 500°K for the decomposition of formic acid and essentially quenched the activity of the nickel catalyst.

IV. DISCUSSION

The most striking result of this work was the long surface residence time of HCOOH (milliseconds) in spite of the low *apparent* activation energy for desorption. The very similar *apparent* first-order rate constants for the desorption of HCOOH from the different catalytic surfaces suggested that these substrates were *similar* during the MBRS experiments below room temperature. These observations are consistent with the flash desorption studies which revealed that below room temperature these surfaces were largely covered with adsorbed formic acid. Below room temperature the Ni(110) and Ni(110) (4 × 5)C surfaces were covered with a monolayer of chemisorbed formic acid, and HCOOH desorption occurred from the saturated surfaces (*3*, *5*). Approximately 10% of the graphite overlayer contained chemisorbed formic acid which dissociated above room temperature (*3*); similar data for the Ni(110)–sulfur system is not available. The presence of chemisorbed HCOOH on these surfaces below room temperature served to weaken the interaction of the HCOOH molecular beam with the underlying substrate and caused the different samples to behave

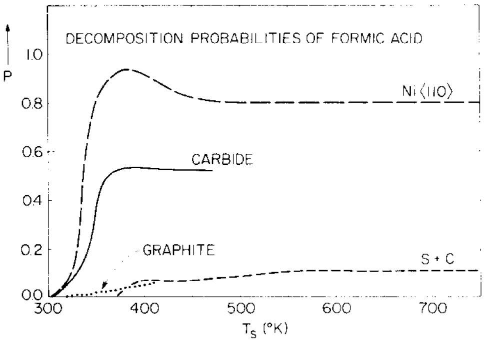

FIG. 4. Decomposition probabilities of formic acid for the various surfaces investigated versus surface temperature.

in an almost indistinguishable manner in this temperature range.

The above observations imply that other substrates containing appreciable amounts of chemisorbed formic acid or passivating layers will also exhibit similar first-order rate constants for the low temperature interactions with molecular beams of formic acid. Recent work on the HCOOH/Ag(110) system agrees with this hypothesis (*8*). The apparent first-order rate constant for the low temperature desorption of HCOOH from Ag(110) in the MBRS mode was found to be within a factor of two of the rate constants observed in the present investigation. Therefore, surfaces with which chemisorb formic acid weakly interacts below room temperature appear to exhibit the same behavior toward a molecular beam of formic acid.

The generally low activation energies probably reflect the weak interactions of the HCOOH molecular beam with the formic acid covered substrates below room temperature. Chemisorbed formic acid exists either as formic anhydride or formate intermediates, both of which have their oxygen atoms buried face down in the surface (*1*–*5*). This implies that the incoming HCOOH molecule would not interact with an energy equal to the heat of sublimation of HCOOH (~11 kcal/mole) since hydrogen bonding, the dominant energetic factor in formic acid sublimation, could not take place. The combination of experimental information gathered (phase-lags, waveforms, and flash desorption) leads to the conclusion that the low activation energies are definitely real and represent the weak interactions experienced by the HCOOH molecular beam, and not some time of flight phenomenon (*9*). The flash desorption experiments demonstrated that HCOOH has binding states above 170°K on these surfaces (*1*–*6*); as this temperature is approached in the present MBRS experiment the waveform amplitudes all rapidly diminish because the HCOOH surface residence times become long relative to the modulation frequency. Furthermore, the continuous change of the waveforms with temperature, as shown in Fig. 1, represent a surface interaction. The low activation energies reflect the weak interaction of gas phase HCOOH with a surface covered by chemisorbed formic acid intermediates.

The extremely low magnitude of the apparent preexponentials, 10^{-4}–10^{-5} $\sec^{-1}$, for the desorption of formic acid from these surfaces has no obvious explanation. They do correspond to the magnitude expected for a second-order desorption step, as might be expected for energy transfer limited processes between adsorbed species, since for our experimental conditions a second-order surface process would exhibit an apparent preexponential factor of about 10^5 $\sec^{-1}$ (*6*). Such a process seems unlikely for adsorbed species, however.

V. CONCLUSION

The similar *long* surface lifetimes of formic acid below room temperature on the Ni(110), Ni(110)–carbide, Ni(110)–graphite, and Ni(110)–sulfur surfaces suggested that the adsorption/desorption mechanisms were the same on these surfaces. Above room temperature the ability of a surface to decompose formic acid was strongly dependent on the nature of the chemilayer. The flash desorption studies exhibited somewhat different formic acid interactions with the series of surfaces than were observed with MBRS and reveal interesting differences between the two experimental techniques, which reflect the importance of adsorbate–adsorbate interactions at higher coverages utilized in flash desorption experiments. These results clearly indicate unusually long surface lifetimes for complex molecules with weak interactions with solid surfaces.

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