

The Adsorption and Decomposition of Formic Acid on Cu{100} and Cu{100}Pt Surfaces using Temperature Programmed Reaction Spectroscopy

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Abstract

The structures formed by adsorbing thin-film platinum, formic acid and oxygen on Cu{100} single crystal are investigated by quantitative low-energy electron-diffraction (LEED) and Temperature Programmed Reaction Spectroscopy (TPRS). Symmetrized Automated Tensor LEED (SATLEED) calculations are used to determine the structure of the formed surface alloys and overlayers. TPRS was used to probe the surface reactivity of the systems studied while surface composition was obtained using Auger Electron spectroscopy (AES). The decomposition of a formate intermediate from a clean Cu{100} surface has been monitored through the use of TPD Spectroscopy.

It has also been evidenced that platinum has a destabilising effect on the formate intermediate. The peak temperature (T_p) for the CO₂ desorption spectra from copper-platinum model surfaces, appear around 40 K lower than those from clean copper. This suggests a much less stable surface alloy compared to the clean surface. In activation energy terms, this destabilisation can be expressed as a 13% decrease in the energy required for the formate to decompose. It was also observed that desorption is much more rapid from the copper-platinum than from clean copper surfaces.

Keywords: Cu{100}, Cu{100}Pt, Formic Acid, TPRS

1. Introduction

The adsorption and decomposition of formic acid at copper surfaces has been intensively studied over the years¹. This is partly because of the key role that formate is believed to play in methanol synthesis and partly because it is an ideal model system. As a result of the attention it has received, the chemistry of the system is well understood. Upon adsorption at 300 K the formic acid dissociates to produce a bidentate formate intermediate, which bonds to adjacent sites on the copper surface through the two oxygen atoms. (Figure 1).

1.1 Theory of Temperature Programmed Desorption (TPD)

TPD as a surface analysis technique was introduced² in 1948. Since adsorption on clean metal surfaces is

generally a non-activated process, the desorption activation energy is then approximately equal to the differential heat of adsorption³. This implies that TPD is a method of measuring the bond energy in adsorption. In addition, the reaction order can be deduced by comparing the peak shapes of TPD spectra.

Compared to other surface techniques, TPD is considered a straightforward and easy to interpret method. Apart from some experimental parameters such as the heating rate β , a typical TPD spectrum provides the desorption peak maximum temperature, T_p and a distinct trace shape that give information about the order of the desorption process. Several methods of analysis of TPD spectra have been described in the literature where the most convenient one is the Redhead method since it provides fairly accurate results and small computation time⁴.

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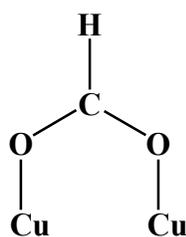


Figure 1. The geometry of formate on a copper crystal.

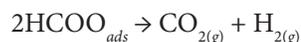
In the Redhead method, the frequency factor is assumed to be independent of coverage. This approximation allows the application of a single equation to calculate E_p , given that the desorption takes place under constant pumping speed and linear heating rate.

$$E = RT_p [\ln (v T_p / \beta) - 3.64]$$

where E is the activation energy in Joules, R is the ideal gas constant of $8.314 \text{ JK}^{-1}\text{mol}^{-1}$, T_p is the desorption peak maximum temperature in Kelvin, v is the frequency factor of 10^{13} sec^{-1} and β is the heating rate in K sec^{-1} .

TPD spectra can also give some information about the relative surface coverage. Provided the pumping speed is constant, the integrated area of a TPD peak is directly proportional to the adsorbate coverage. Therefore, a method of calibration of the mean surface coverage can be obtained by comparing the integrated area under the TPD peak for surfaces with different exposures. Nowadays, TPD is widely used as a complementary method in studying surface structure and investigating simple chemical reactions on surfaces especially when gas adsorption behaviour is highly dependent on the constituents and morphology of surfaces.

It is generally accepted that the formate decomposes at $\sim 470 \text{ K}$ to yield carbon dioxide and hydrogen⁵.



This has been evidenced through the use of Temperature Programmed Desorption Spectroscopy. Following the adsorption of formic acid on a $\text{Cu}\{100\}$ crystal, coincident peaks representing the evolution of CO_2 and H_2 are observed at $\sim 470 \text{ K}$ ⁶. Furthermore, the behaviour of formic acid when adsorbed on a $\text{Pd}/\text{Cu}\{110\}$ surface has also been studied. It has been observed⁵, that palladium has a destabilising effect on the formate intermediate.

The present work seeks to further examine the kinetics of the adsorption and decomposition of formic acid on

a copper single crystal surface. In addition, the effect that platinum has on the stability of the formate intermediate is also investigated.

Temperature Programmed Desorption Spectroscopy is employed in order to do so. A $\text{Cu}(100)$ crystal is used for these studies, and platinum model surfaces were formed by depositing varying amounts of platinum onto the crystal.

In a TPD experiment, an adsorbate, generally in its gaseous form, is dosed onto the surface to be studied at a certain pressure for a certain time. Surface exposure is usually quoted in Langmuirs (L) where $1 \text{ L} = 10^{-6} \text{ Torr sec}$. A linear temperature ramp is then applied to the sample where the amount of desorbed species is monitored as a function of temperature. Figure 2, shows a schematic diagram of a simple TPD experiment set-up.

In resistive heating, which is the usual method of heating, an electric current is applied to the sample support wires. The heating rate β is the most important experimental variable in TPD experiments. Higher β generally shifts the desorption peak to a higher temperature. Analysis of TPD spectra requires that β is linear over the temperature range of interest. Typical β values are in the range $1\text{--}10 \text{ K/s}$.

Depending on reaction products and level of accuracy needed, mass spectrometers vary in specification. The most common one is the quadrupole mass spectrometer (QMS). Different e/m fragments can be monitored upon desorption simultaneously by “multiplexing”. The distance between the sample and the detector (QMS) is minimised to ensure maximum detection efficiency but it is important to keep it fixed if integrated area of different TPD spectra are to be compared with each other.

Since interference from gases present in the background vacuum and variable sensitivity of the QMS

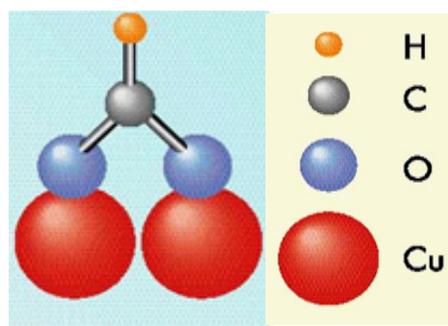


Figure 2. view of the proposed bonding geometry of the formate intermediate on $\text{Cu}\{100\}$.

at different pressure values are some major problems in TPD experiment, it is important to maintain a constant base pressure in the vacuum chamber when TPD spectra are recorded. In some cases where background gases interfere strongly with the recorded spectra, a background spectrum may be subtracted.

Adsorption of various species on clean and alloyed Cu single crystal surface has been studied extensively by TPD^{6,7}. Formic acid (HCOOH) and carbon monoxide (CO) are the most common simple gases used to probe surface reaction reactivity.

Formic acid is the simplest carboxylic acid. It forms a strong, stable bidentate formate intermediate on copper surfaces. The formate is stable up to approximately 450 K on Cu{100} before it decomposes to yield CO₂ and H₂. It has been found that this decomposition follows first order kinetics⁸.

Madix and co-workers⁹ were the first to study formic acid TPD from Cu in 1980. They found that formic acid adsorbs on a Cu{110} surface to produce a formate species. Using TPD¹⁰, investigated the adsorption and decomposition of formic acid on Cu{110}. A structural study of formate on Cu{111} by Sotiropoulos using normal incidence, X-ray standing wavefield absorption

(NIXSW) suggested that the oxygen atoms of the formate were located in a top site and with the formate bridging two copper atoms¹¹. Figure. 2, shows the proposed bonding of the formate intermediate on Cu{100}.

2. Experimental

Experiments were performed in a stainless steel ultra-high vacuum chamber Figure 3. The pressure of the chamber was maintained in the low 10⁻¹⁰ Torr region by means of an ion pump and a titanium sublimation pump. The chamber was equipped with a quadrupole mass spectrometer, an argon ion bombardment gun and 4-grid Low Energy Electron Diffraction (LEED) optics. The mass spectrometer is employed as detector for the temperature programmed desorption measurements. It is also utilised for residual gas analysis, and for checking the purity of the admitted formic acid.

Cleaning of the crystal involved repeated cycles of argon -ion bombardment, followed by annealing to ~700 K. The surface crystallography was monitored by low-energy electron diffraction (LEED). A clean copper surface is indicated by the appearance of sharp, intense symmetric diffraction spots with a low background. The achievement

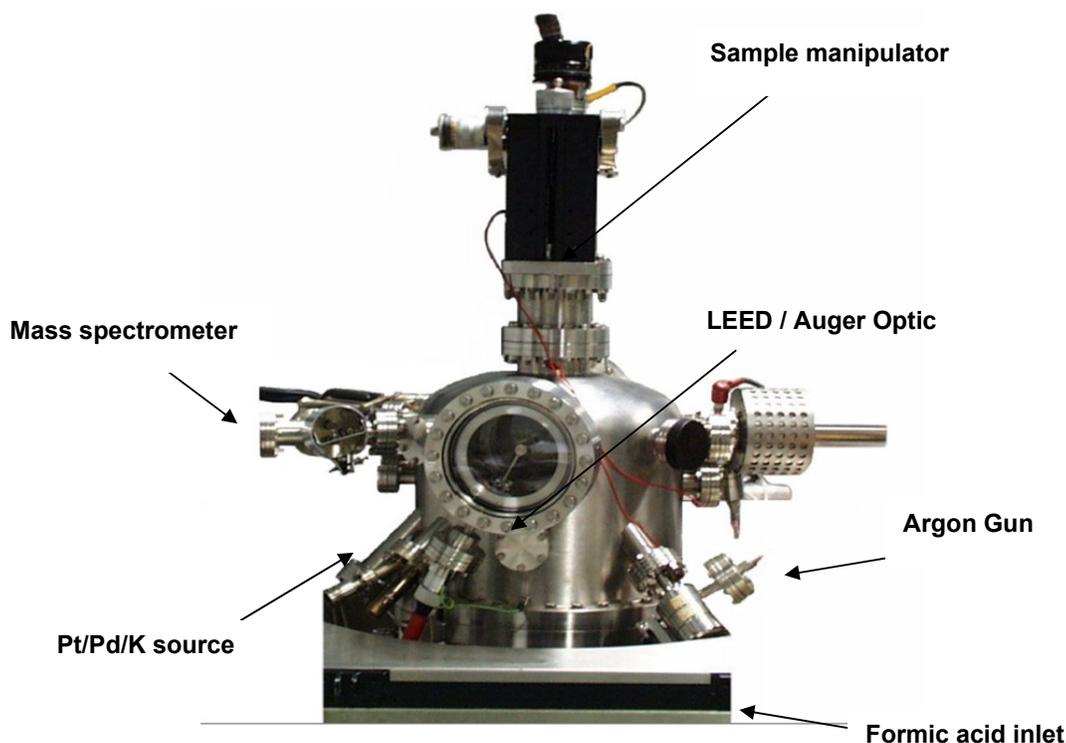


Figure 3. Stainless steel ultra- high vacuum chamber.

of good quality platinum-copper model alloy surfaces was confirmed by the observation of a good $c(2 \times 2)$ pattern. Platinum was dosed from a home-made evaporator consisting of a 0.3 mm diameter tungsten filament around which a 0.125 mm Pt wire was wound. The filament was mounted on a titanium sublimation pump feed through, and fitted with a stainless steel shield. Evaporation was achieved via the resistive heating of the filament.

The formic acid (97% purity, Aldrich chemicals) was purified by several freeze-pump-thaw cycles, in order to remove any dissolved gases. Dosing was performed through an all-metal leak valve with exposure measured with an uncalibrated Bayard-Alpert ionisation gauge. Exposures are quoted in Langmuirs (1 Langmuir = 10^{-6} Torr sec). The Cu(100) crystal was mounted via suspension between stainless steel blocks by tantalum wires. The crystal was heated resistively, in linear fashion, by passing a direct current through the wires. A thermocouple junction spot-welded to the edge of the sample provides a means of measuring the sample temperature. The crystal is rotatable about the vertical chamber axis to position it for LEED analysis, argon ion bombarding, platinum evaporation and TPD measurements.

3. Results and Discussion

The Cu{100} surface was initially exposed to increasing amounts of formic acid, in an attempt to determine how the desorption peaks vary with coverage. The following sets of spectra were obtained. (Figure 4).

CO₂ evolution was monitored by tuning the mass spectrometer to detect species of mass 44-monitored. H₂

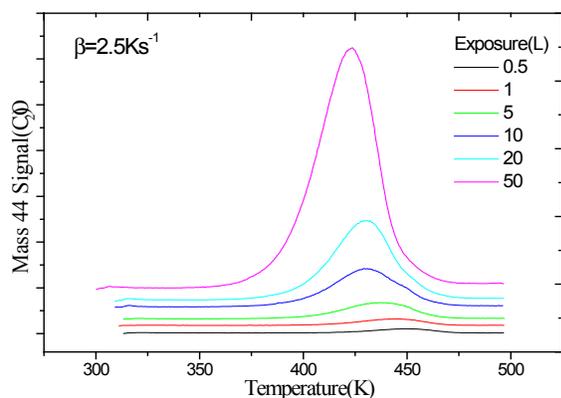


Figure 4. Stack plot of CO₂ desorption spectra obtained, following exposure to 0.5, 1.0, 5, 10, 20 and 50 L formic acid on Cu{100}.

evolution was also observed at a coincident temperature to the CO₂. However, due to the inference of residual hydrogen in the chamber, poor quality mass 2 spectra were obtained. Hence, only CO₂ desorption was followed in this work.

It can be seen from the above plots that as the surface is exposed to increasing amounts of formic acid, the desorption peak increases in intensity, but it is also noted that the peak temperature for maximum desorption (T_p), shifts to lower temperatures.

It shifts from 458 K for an exposure of 0.5 L to 433 K for 50 L. The activation energies for each exposure of formic acid were calculated using the Redhead equation and tabulated in Table 1.

It is generally accepted that the desorption of formate from single crystal surfaces is a first order process⁵, and this is supported by the asymmetric shape of the peak observed. Hence, the following form of the Redhead equation was used for evaluating the activation energy:

$$E_d = RT_p [\log_e(AT_p/\beta) - 3.46]$$

where: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, β is the heating rate and A is assumed to be 10^{13} s^{-1} .

The shift of the peak maxima to lower temperatures as a function of increasing exposure does not support the proposition of first-order kinetics. It is proposed however, that this shift is as a result of repulsive lateral interactions between the adsorbed molecules. It is well understood that repulsive interactions lead to the destabilisation of the adsorbate. This is illustrated by the decrease in desorption energies, as given by the Redhead method.

In an attempt to investigate the effect of platinum on the stability of the formate intermediate, platinum model surfaces were formed by depositing varying amounts of platinum onto the Cu{100} crystal. The amounts of platinum decided upon for this study were 0.5, 1.0 and 1.5 monolayers. Figure 5 illustrates the spectra obtained

Table 1. Activation Energies for various Exposures of formic acid on pure Cu{100}

| Exposure (L) | E_d (KJ mol ⁻¹) |
|--------------|-------------------------------|
| 0.5 | 121 |
| 1 | 119 |
| 1 | 118 |
| 10 | 116 |
| 20 | 115 |
| 50 | 114 |

following adsorption of 0.5, 1.0, 5.0 and 20 L formic acid on Cu{100} surface alloyed with 0.5 ML Pt.

A comparison of the spectra obtained for the above system and for the pure copper system yields striking similarities. The peak temperatures are almost identical, as are the peak shape, and again there is a downward shift of T_p with increasing exposure. A possible explanation for these observations is that the desorption experiments were performed the day after the layer was deposited. It is extremely likely that during this period, the platinum diffused from the surface into the bulk. Hence, it would be wrong to conclude from the above spectra that 0.5 ML Pt has no effect on the stability of the formate. In contrast, the desorption spectra obtained when 1.0 ML Pt was deposited, shows that platinum results in a considerable destabilisation of the formate Figure. 6.

The presence of 1.0 ML Pt leads to significant differences in the TPD spectra obtained, relative to those of pure copper {100}. Considering the curve representing desorption of 20 L for example from pure Cu{100}, the T_p for this exposure was 438 K compared to 393 K with 1.0 ML Pt.

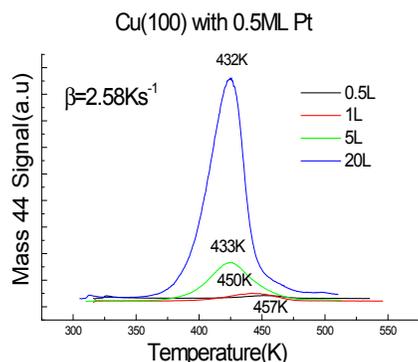


Figure 5. Stack plot of CO₂ desorption spectra obtained from Cu{100} with 0.5 ML Pt.

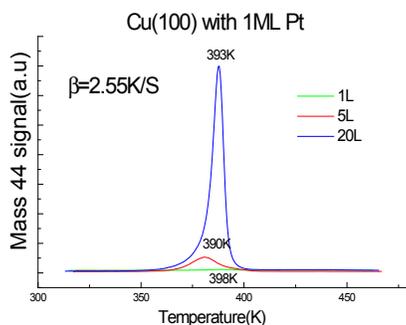


Figure 6. Stack Plot of CO₂ spectra obtained following adsorption of 1.0, 5.0 and 20 L formic acid from Cu{100} alloyed with 1.0 ML Pt.

In activation energy terms, the decrease corresponds to a reduction of 12 KJ mol⁻¹. Hence, the 1.0 ML Pt has led to considerable destabilisation of the formate. It is also to be noted, that 1 ML Pt results in a much narrower peak than that afforded with pure Cu.

It is difficult to deduce from the above spectra whether there exists any lateral interactions between the adsorbed molecules. There is no systematic shift of T_p in this case. A repeat of this experiment incorporating additional exposure of formic acid is necessary, in order to clarify the existence of lateral interactions. The high quality of spectrum obtained for 20 L formic acid on Cu{100} with 1 ML Pt, (little noise) allows application of the Leading Edge Method. Figures 7, 8 illustrate the resulting

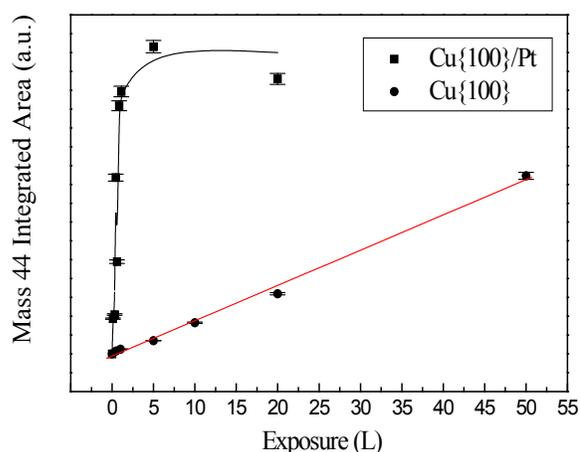


Figure 7. Integrated area of mass 44(CO₂) desorption from both Cu{100} and Cu{100}-c(2x2)-Pt surfaces as function of formic acid exposure.

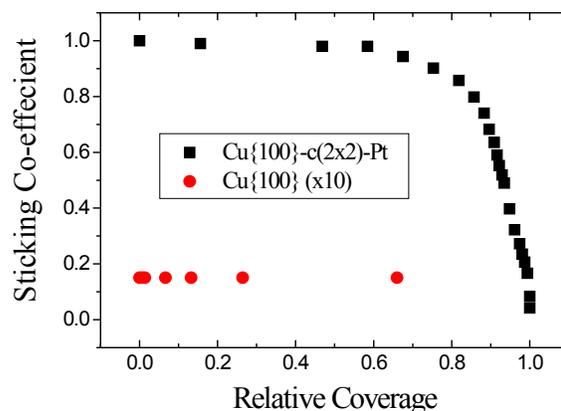


Figure 8. Variation of formic acid sticking co-efficient with coverage on both Cu(100) and a Cu{100}-c(2x2)-Pt surface of intermediate Pt loading.

coverage-dependent dissociative sticking co-efficient for both surfaces.

As HCOOH exposures were measured using a Bayard-Alpert ionisation gauge absolute sticking co-efficient may be in error. A formate saturation coverage of 0.5 ML (7.6×10^{14} molecules /cm²) has been assumed on both surfaces.

Knowing that the slope of these plots is equivalent to $(-E_d)/R$, E_d could be calculated. It was found that when there was a coverage decrease of 8%, the desorption energy was found to be 124 kJmol⁻¹, and in the case of 1 %, the energy was found to be 100 KJ mol⁻¹. Values were also obtained for intermediate percentage decreases in coverage. These are tabulated in Table 2, (Pre-exponential factors (A) are also quoted. These were determined from the intercept of the plots, as the intercept is equivalent to Ln A).

It can be seen that as the % of the leading edge from which the data taken decreases, the values obtained for the desorption energies approach that given by the Redhead method (104 K).

Following deposition of 1.5 ML Pt on the Cu{100} crystal and dosing with 0.5, 1.0, 5.0 and 20 L formic acid, the TPD spectra shown in Figure 9. were obtained.

Again, it is to be noted that T_p is much lower than those observed on pure Cu{100}.

Also, the desorption peak are much narrower. Another interesting observation is that in this case, the peak temperature appears to increase with increasing exposure to adsorbate. This is indicative of attractive lateral interaction. However, this cannot be conclusively stated because of the singe of the shift.

Considering the lowest and highest exposures, an overall shift of 7 K is observed. It is impossible to make a conclusive deduction because the peak temperature is within a 5 K error.

Table 2. Desorption energies and pre-exponential factors obtained using the Leading Edge Method, for 20 L HCOOH on Cu{100} with 1.0 ML Pt

| %Decrease in Coverage HCOOH | Desorption Energy (KJmol ⁻¹) | Pre-exponential Factor |
|-----------------------------|--|------------------------|
| 1 | 100 | 4.5×10^5 |
| 2 | 107 | 4.6×10^6 |
| 4 | 114 | 5.3×10^7 |
| 6 | 120 | 3.6×10^8 |
| 8 | 124 | 1.3×10^9 |

Utilising the Redhead Method, and assuming a pre-exponential factor of 10^{13} , average desorption energy of 105kJ mol⁻¹ was obtained for the 1.5 ML surface. As well as providing information regarding the stability of the formate intermediate on the various surfaces, the TPD experiments also allow the calculation of the sticking probability of formic acid.

Figure 10. shows plots of the integrated areas under the desorption peak obtained on clean Cu{100} (A) and on the 1.5 ML Pt surface.(B)

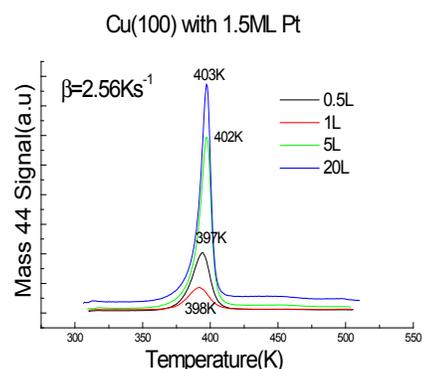


Figure 9. CO₂ desorption spectra obtained from Cu{100} with 1.5 ML Pt

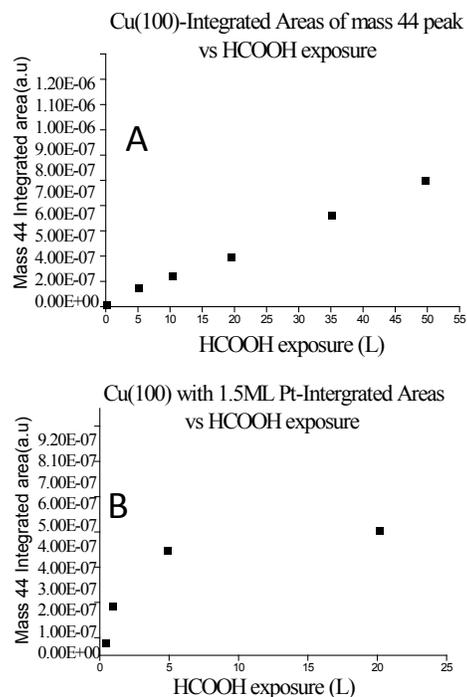


Figure 10. Plots of the integrated areas under the desorption peak obtained on clean Cu{100} (A) and on the 1.5 ML Pt model system.(B)

The linearity of the Cu{100} plot indicates the crystal does not become saturated with formic acid until it is exposed to at least 50 L. It cannot be said with certainty that saturation occurs upon exposure to 50 L. However, the linearity is a sign that precursor adsorption takes place. This means that if a formic acid molecule collides with the surface at a filled adsorption site, it forms a weak Van der Waals type bond to the surface and diffuses for some finite length of time until it finds a vacant site and becomes chemisorbed.

In the case of the 1.5 ML Pt, it can be deduced from the plot that saturation occurs upon exposure to 10 L formic acid. Figure 11, illustrates the relative sticking probability of formic acid on this surface.

It is likely that Langmuir adsorption is occurring in the case, whereby an adsorbate molecule, which collides with the surface at a filled adsorption site, rebounds back into the gas phase, and re-collides until it finds a vacant site.

Absolute sticking probabilities were calculated using the relationship:

$$S = \frac{\text{No. of molecules adsorbed per cm}^2 \text{ surface}}{\text{No. of molecules that collide with 1 cm}^2}$$

The number of molecules that were adsorbed by 1 cm² surface was calculated using the plots of integrated area vs exposure. The number of molecules that collide with 1 cm² (z) was determined from the equation:

$$Z = [p/(2\pi mkT)]^{1/2}t$$

Where p = pressure of dosing (Ncm⁻²)

t = dosing time (s)

m = molecular mass in kg molecule⁻¹

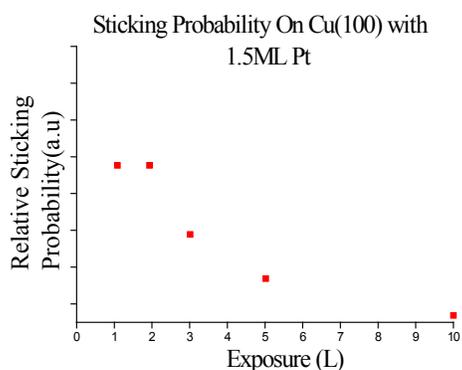


Figure 11. Relative Sticking Probability of formic acid on Cu{100} with 1.5 ML Pt.

T = temperature of chamber in K

K = Boltzmann constant, in JK⁻¹

It was found as expected that the sticking probability of formic acid on pure Cu{100} remained constant, regardless of exposure. This is because of the precursor type adsorption. A value of 0.05 was obtained.

The sticking probability on the 1.5 ML Pt surface was found to be much higher, and decreased with increasing exposure. 0.5 L formic acid has a sticking probability of 0.67 and 10 L has a sticking probability of 0.25. This is as expected because as more formic acid is put on, there are fewer vacant adsorption sites. Hence it is less likely that the later molecules will adsorb.

Figure 12 provides a comparison of the TPD spectra obtained for saturation coverage on each of the four surfaces studied. (It is assumed that pure Cu{100} saturates upon exposure to 50 L formic acid).

This plot provides a clear illustration of the effect of platinum on the stability of the formate intermediate. It is evident that the platinum de-stabilises the intermediate. This is shown by the shift of T_p to a lower temperature as the amount of platinum was increased. (There is doubt about the validity of the result obtained for the 1.0 ML and the 0.5 ML surfaces, the T_p is expected to fall between that of 0.5 ML and 1.5 ML).

Furthermore, Figure. 12 clearly illustrates the difference in peak widths for the four surfaces. It is evident that the platinum surface gives rise to much narrower peaks than clean copper. Narrow peaks are indicative of rapid desorption, hence it can be stated that for some reason the presence of platinum leads to an increase in the rate at which the adsorbed formate desorbs.

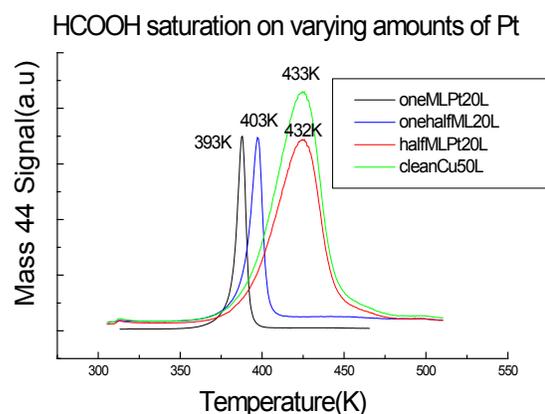


Figure 12. CO₂ desorption spectra obtained following saturating pure Cu{100}, and the 0.5 ML, 1.0 ML and 1.5 ML Pt surfaces with formic acid.

The presence of repulsive lateral interaction on the clean Cu{100} surface as evidenced by the TPD spectra, shown in Figure 13, is a reasonable proposition, considering the geometry of the formate ion on the copper surface.

The oxygen's of neighbouring molecules repel each other due to their electro- negativity and their competition for electron density from the copper. This repulsion is much stronger than any hydrogen bonding that may exist between neighbouring formates. This repulsive behaviour explains the 7 kJ mol⁻¹ decrease in desorption energy, considering the adsorption of 0.5 L and 50 L formic acid. In relation to the other surfaces, it has been proposed that following deposition of platinum, the surface structure consists of a pure copper layer capping a mixed CuPt alloy⁷⁻¹². This structure would not easily account for the remarkable differences observed between the clean Cu{100} TPD spectra and those of the copper-platinum model surfaces.

Further investigation into the copper-platinum surfaces, using CO as a probe, has led to the identification of tiny platinum clusters. It is believed that these clusters occupy around 5% of the outermost layer. One possible explanation for the observation made on the copper-platinum surface, is that the platinum clusters promote the desorption of formate. It is proposed that the adsorbed molecules diffuse towards the platinum clusters, where they undergo rapid decomposition. This process would account for the lower desorption energy and narrower peak of the copper-platinum surfaces. In addition, the affinity of the formic acid for the Pt clusters would explain why the sticking probability is greater on the copper-platinum surface than on the clean copper.

The kinetic parameters deduced from the TPD spectra using the Redhead and Leading Edge Method, have been reported as desorption energies and pre-exponential factors. It is important to highlight the fact that the desorption energy corresponds to the activation energy required for the decomposition of formate, and that the

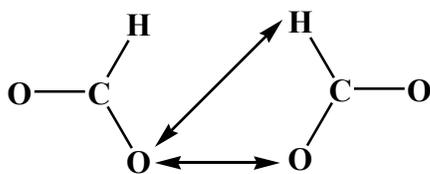


Figure 13. Geometry of formate on copper, illustrating lateral interactions.

pre-exponential factor is of the same order of magnitude as the molecular vibrational frequency. Therefore, it corresponds to the frequency with which the formate molecule goes to the transition state, where decomposition becomes favoured.

The values of the E_d and A obtained from the Leading Edge Method as applied to the 1.0 ML Pt system, exhibit a compensatory effect, i.e. E_d and A vary in concert to fulfil the conditions of the rate constant:

$$k_d = A \exp(-E_d/RT).$$

where E_d is the activation energy for desorption, A is a pre-exponential factor. A maximum is observed because, although k_d increase exponentially with temperature, the surface coverage decreases simultaneously^{13,14}.

4. Conclusion

The decomposition of a formate intermediate from a clean Cu{100} surface has been monitored through the use of TPD Spectroscopy. CO₂ evolution was observed ~440 K. The presence of repulsive lateral interactions between the adsorbates on the surface has been identified, through the shift of peak temperature to lower value, as the surface was exposed to increasing amounts of formic acid. The T_p for 0.5L was observed at 458 K, while that for 50 L appears at 443 K. This shift means that the decomposition energy is reduced by 6%.

It has also been evidenced that platinum has a destabilising effect on the formate intermediate. Peak temperature (T_p) for the CO₂ desorption spectra from copper-platinum model surfaces, appear around 40 K lower than those from clean copper this suggests a much less stable surface alloy compared to the clean surface. In activation energy terms, this destabilisation can be expressed as a 13% decrease in the energy required for the formate to decompose. It was also observed that desorption is much more rapid from the copper-platinum than from clean copper. More study is needed to fully understand these results.

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