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THE OXIDATION OF H_2CO ON A COPPER(110) SURFACE

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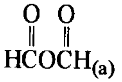
The oxidation of $H_2C^{16}O$ by adsorbed ^{18}O was studied on an Cu(110) sample by temperature programmed reaction spectroscopy. Formaldehyde exchanged its oxygen with surface ^{18}O upon adsorption to yield $H_2C^{18}O_{(a)}$ and $^{16}O_{(a)}$. Formaldehyde was also oxidized by surface ^{16}O and ^{18}O atoms to H_2COO which subsequently released one of the hydrogen atoms to form HCOO. The evolution of H_2 from the Cu(110) surface was desorption limited, and the low pre-exponential factor for the recombination of the surface hydrogen atoms suggested stringent requirement on the trajectories of the colliding partners. The formate was very stable and dissociated at elevated temperatures to simultaneously yield H_2 and CO_2. The surface concentration of ^{18}O exerted a pronounced affect on the activity of the oxidation of formaldehyde on Cu(110).

1. Introduction

In the course of our previous work studying the reactions of small molecules on single crystal surfaces the importance of the intermediates

$HCOO_{(a)}$,



$$\overset{O}{\overset{\|}{C}}H\overset{O}{\overset{\|}{C}}OCH_{(a)}$$

and $CH_3O_{(a)}$

has become quite clear [1–4]. These intermediates are readily formed from HCOOH and CH_3OH on a variety of surfaces, and the question arises whether or not they can be formed via other reactants, since they are very stable intermediates. As this question relates to the oxidation of alcohols and aldehydes on metal surfaces, we have examined the oxidation of H_2CO on a Cu(110) surface. In addition the adsorption/desorption behavior of H_2O, C_2H_4, H_2CO, and D atoms was examined.

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2. Experimental

The oxidation of H_2CO on Cu(110) was studied using UHV techniques [1,2]. Enriched oxygen (99% $^{18}O_2$) was purchased from Bio. Rad. Laboratories and was introduced into the background of the UHV chamber through a variable leak valve. During preadsorption of $^{18}O_2$ on the surface, an oxygen background pressure of 1×10^{-8} Torr was maintained and only the exposure time was varied. The copper sample was kept at ~22°C during the adsorption of oxygen. The oxygen exposure was varied from 0 to 2 L (1L = 1 Langmuir is defined as 1×10^{-6} Torr sec of oxygen exposure), and the surface coverages of oxygen were determined by AES. Details of the AES calibration procedure for the Cu(110) surface are to be found elsewhere [3]. A 1 L exposure to $^{18}O_2$ and 2 L $^{18}O_2$ yielded 9 and 17% of an adsorbed oxygen monolayer on the surface, respectively. High purity paraformaldehyde (mp 163–165°C) was purchased from Aldrich Chemical Company and was outgassed by prolonged pumping at 85°C. The formaldehyde vapor obtained by heating the solid paraformaldehyde to ~60°C was used directly for the adsorption studies on copper. The composition of the formaldehyde vapor was analyzed with the mass spectrometer and was found to contain only trace amounts of CH_3OH.

AES analysis revealed that the Cu(110) surface predosed with 1 L $^{18}O_2$ was free of oxygen subsequent to 100 sec exposure of formaldehyde. All of the oxygen was consumed in the surface reaction, since oxygen was not observed to otherwise desorb from the Cu(110) surface. Auger analysis at the end of the day revealed the presence of ~10% of a surface carbon monolayer. This amount of surface carbon did not influence the reactions investigated because the first flash decomposition spectrum of the day was always reproduced at the end of the day. A heating rate of ~5 K sec^{-1} was employed throughout this investigation.

3. Results

The product distribution subsequent to the adsorption of $H_2C^{16}O$ on a Cu(110) surface that was predosed with 1 L of $^{18}O_2$ is presented in fig. 1. The first species to desorb upon heating the single-crystal sample was the parent molecule, $H_2C^{16}O$. Some of the formaldehyde exchanged its oxygen with surface oxygen-18 to form $H_2C^{18}O$ and exhibited a desorption spectrum that was essentially identical to $H_2C^{16}O$. The remainder of the products observed in fig. 1 were related to the direct oxidation of formaldehyde by surface oxygen-18.

The simultaneous evolution of $C^{16}O^{18}O$, $C^{16}O^{16}O$, and H_2 at about 470 K resulted from the decomposition of two types of formate intermediates, $HC^{16}O^{18}O$ and $HC^{16}O^{16}O$; because previous results with HCOOH showed that the formate intermediate dissociated about 470 K on Cu(110) to yield H_2 and CO_2 (see table 1). The notation $A(\alpha)/B$ refers to the α state or desorption peak for gas A following adsorption of gas B. The H_2 peak observed at about 336 K was desorption limited,

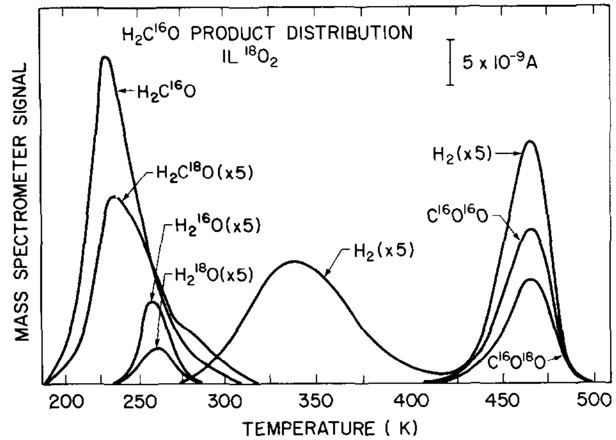


Fig. 1. Temperature programmed desorption spectrum following $H_2C^{16}O$ adsorption at 180 K on a Cu(110) surface that was predosed with 1 L $^{18}O_2$ at 295 ± 10 K. The $H_2C^{16}O$ exposure was 100 sec. These curves are uncorrected for detection sensitivities.

since D_2 was also shown to desorb from the Cu(110) surface with the same peak temperature (see table 1) subsequent to the adsorption of D atoms. Since deuterium (and hydrogen) will not chemisorb on a copper surface the ionizer of the mass spectrometer was used to generate a source of D atoms from a background of $\sim 10^{-6}$ Torr of deuterium. Very small amount of $H_2{}^{16}O$ and $H_2{}^{18}O$ were formed below room temperature, and these products desorbed at about 260 K. Trace amounts of $H_2C^{16}O$ and CH_3OH were observed at approximately 365 K, not shown in fig. 1, and originated from the small amount of CH_3OH generated by heating the

Table 1
The interaction of simple molecules with the oxygen-free Cu(110) surface

	T_p (K)	E (kcal/mole)	ν (sec^{-1})	E[a] (kcal/mole)
CO/CO	223	14	4×10^{13}	13.5
CO/CO_2	223	14	4×10^{13}	13.5
$H_2O(\alpha)/H_2O$	235	–	–	14.2
$H_2O(\beta)/H_2O$	285	–	–	17.3
C_2H_4/C_2H_4	224	–	–	13.5
H_2CO/H_2CO	225	–	–	13.5
D_2/D_{atoms}	336 [b]	12 ± 1 [b,c]	$1 \times 10^{-7 \pm 1}$ [b,c]	–
$H_2 + CO_2$/HCOOH	470	32 ± 1	$8 \pm 2 \times 10^{13}$	29.0

[a] Assuming that for first-order process $\nu = 1 \times 10^{13}$ sec^{-1}.
[b] 2nd order process (T_p is coverage dependent and ν has units of cm^2/sec^{-1}).
[c] Kinetic parameters calculated from plot of $\ln(R/C^2)$ versus $1/T$ [2].

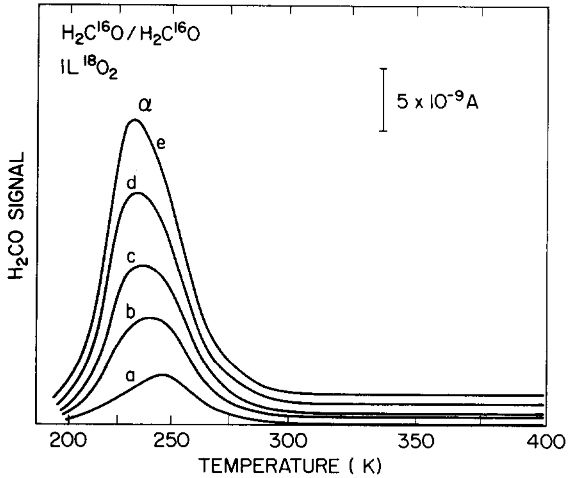


Fig. 2. The $H_2C^{16}O$ desorption spectra subsequent to the adsorption of $H_2C^{16}O$ at 180 K on a Cu(110) surface presdosed with 1 L $^{18}O_2$ at 295 ± 10 K. The $H_2C^{16}O$ exposures were: (a) 5 5 sec, (b) 13 sec, (c) 25 sec, (d) 50 sec, and (e) 100 sec.

paraformaldehyde source as shown by previous studies with CH_3OH. No other flash decomposition products were observed; in particular, carbon monoxide, methane, methyl formate, and methylal were absent from the spectrum.

3.1. $H_2C^{16}O/H_2C^{16}O$

The flash desorption spectra of $H_2C^{16}O$ from a partially oxidized (1 L $^{18}O_2$) Cu(110) surface is shown in fig. 2 as a function of formaldehyde coverage. The $H_2C^{16}O(\alpha)/H_2C^{16}O$ peak maxima shifted about 10 K with increasing coverage, and a careful examination of the desorption spectra suggested that two formaldehyde binding states existed at ~240 K. The overlap of the two formaldehyde peaks prevented the calculation of the kinetic parameters for the desorption of formaldehyde from the Cu(110) surface. If a frequency factor $\nu \equiv 10^{13}$ $\sec^{-1}$ was assumed, then an activation energy of 14.5 kcal/mole was obtained for the first order desorption of formaldehyde from the partially oxidized Cu(110) surface.

3.2. $H_2C^{18}O/H_2C^{16}O$

The $H_2C^{18}O$ desorption spectra from the Cu(110) surface that was predosed with 1 L of $^{18}O_2$ was essentially identical to the $H_2C^{16}O$ desorption spectra from the same surface (compare figs. 2 and 3). Both products exhibited the same binding states as a function of coverage; the $H_2C^{18}O(\alpha)/H_2C^{16}O$ peak maxima also shifted about 10 K with increasing coverage. These results suggested that $H_2C^{16}O$

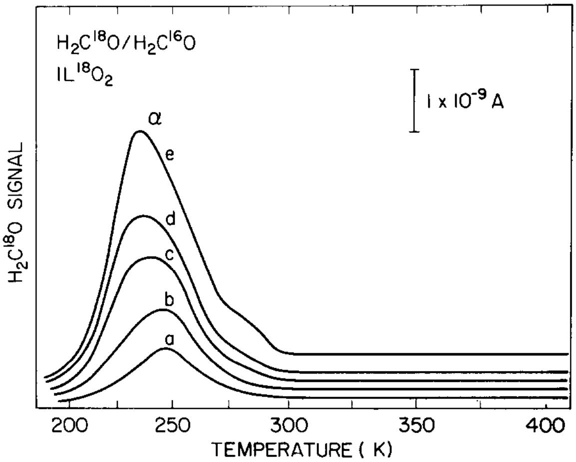


Fig. 3. The $H_2C^{16}O$ temperature programmed spectra subsequent to the adsorption of $H_2C^{16}O$ at 180 K on a Cu(110) surface predosed with 1 L $^{18}O_2$ at 295 ± 10 K. The $H_2C^{16}O$ exposures were: (a) 5 sec, (b) 13 sec, (c) 25 sec, (d) 50 sec, and (e) 100 sec.

exchanged its oxygen with surface oxygen-18 upon adsorption since both spectra were essentially identical throughout the flash desorption. The oxygen-16 atoms that were released in this exchange during the adsorption process were therefore available for interaction with other formaldehyde molecules on the Cu(110) surface.

3.3. $H_2/H_2C^{16}O$

The desorption of $H_2/H_2C^{16}O$ from the partially oxidized Cu(110) surface is presented in fig. 4 as a function of formaldehyde exposure. The $H_2/H_2C^{16}O$ desorption spectra exhibited two peaks: γ and δ. The $H_2(\gamma)/H_2C^{16}O$ peak maxima shifted to lower temperatures with increasing coverage, and this suggested that the desorption of hydrogen from this state was a non-linear process. This peak was analyzed by isothermal analysis [1], and the reaction order was found to be $n = 2.0 \pm 0.2$. This analysis also yielded the rate constant for this second-order process to be:

$$k_{H_2(\gamma)/H_2C^{16}O} = 1 \times 10^{-6\pm1} \exp\left(-\frac{13.2 \pm 0.2 \text{ kcal/mole}}{RT}\right)\frac{\text{cm}^2}{\text{sec}}.$$

The desorption of D_2 subsequent to the adsorption of D atoms on the Cu(110) surface was also investigated, see table 1, and the second-order rate constant was found to be:

$$k_{D_2/D_{\text{atoms}}} = 1 \times 10^{-7\pm1} \exp\left(-\frac{12.1 \pm 1.0 \text{ kcal/mole}}{RT}\right)\frac{\text{cm}^2}{\text{sec}}.$$

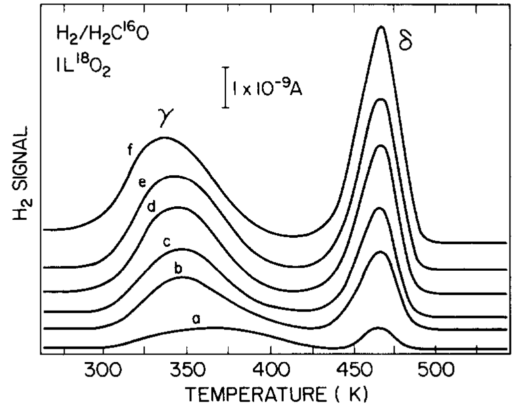


Fig. 4. H_2 production subsequent to $H_2C^{16}O$ oxidation on Cu(110). The Cu(110) surface was oxidized by 1 L $^{18}O_2$ at 295 ± 10 K prior to adsorption of $H_2C^{16}O$ at 180 K. The $H_2C^{16}O$ exposures were: (a) 1 sec, (b) 5 sec, (c) 13 sec, (d) 25 sec, (e) 50 sec, and (f) 100 sec.

The uncertainty in the above pre-exponential factors arose from the uncertainty in the coverages of the hydrogen and deuterium atoms on the Cu(110) surface. The rate constants calculated above are the same, within experimental error, and demonstrated that $H_2(\gamma)/H_2C^{16}O$ was desorption limited. The $H_2(\delta)/H_2C^{16}O$ peak was, however, a reaction limited peak.

The $H_2(\delta)/H_2C^{16}O$ peak temperature was constant for over a ten-fold increase in coverage, which suggested that the rate-limiting-step was a first-order surface process. The peak maxima at ~470 K also coincided with the $C^{16}O^{18}O/H_2C^{16}O$ and $C^{16}O^{16}O/H_2C^{16}O$ peak maxima. The decomposition of the formate intermediate to H_2 and CO_2 was observed during the interaction of HCOOH with Cu(110) and occurred at ~470 K. It was concluded from these observations that the appearance of $H_2(\delta)$, $C^{16}O^{18}O$, and $C^{16}O^{16}O$ at ~470 K was due to the decomposition of two different formates: $HC^{16}O^{18}O$ and $HC^{16}O^{16}O$.

The ratio of the hydrogens evolved from the $H_2(\gamma)$ and $H_2(\delta)$ peaks was always approximately unity. This suggested that most of the hydrogen released when formaldehyde was oxidized to the formate intermediate desorbed from the $H_2(\gamma)/H_2C^{16}O$ peak.

3.4. $H_2{}^{16}O$ and $H_2{}^{18}O/H_2C^{16}O$

Trace amounts of water, $H_2{}^{16}O$ and $H_2{}^{18}O$, were formed subsequent to the adsorption of $H_2C^{16}O$ on the Cu(110) surface predosed with 1 L of $^{18}O_2$, see fig. 1. Two binding states for H_2O exist on Cu(110) with peak temperatures of 235 and 285 K (see table 1), but the water peaks observed in this reaction occurred at ~260 K. The slightly different peak temperature observed in this study suggested that the bond between the water molecules and the copper substrate was perturbed by the presence of the much stronger surface bond of the formate intermediate. The water peaks at ~260 K revealed that hydrogen atoms were already present on the Cu(110) surface at this temperature although molecular hydrogen itself could not desorb until higher surface temperatures.

3.5. Oxygen variation studies

The influence of oxygen exposure on the product distribution observed for the oxidation of $H_2C^{16}O$ on the Cu(110) surface is presented in fig. 5. The oxygen-free Cu(110) surface was relatively inactive for the dissociative adsorption of formaldehyde and only a small amount of $C^{16}O^{16}O$ and H_2 was formed. All of the reaction products exhibited a marked dependence on the surface concentration of oxygen, and the magnitudes of the various product signals increased dramatically as the Cu(110) surface was oxidized.

The $H_2C^{18}O$ signal (which originated from the exchange process involving $H_2C^{16}O$ and an ^{18}O atom) and the $C^{16}O^{16}O$ signal (which originated from the oxidation of $H_2C^{16}O$ by an ^{16}O atom released in the exchange process) displayed the same qualitative behavior as a function of oxygen exposure, see fig. 5. The ratio of the $H_2C^{18}O/C^{16}O^{16}O$ signals, except on the surface not exposed to ^{18}O, was approximately unity when the signals were corrected for their different mass spectrometer sensitivities. Thus observation revealed that almost every ^{16}O atom

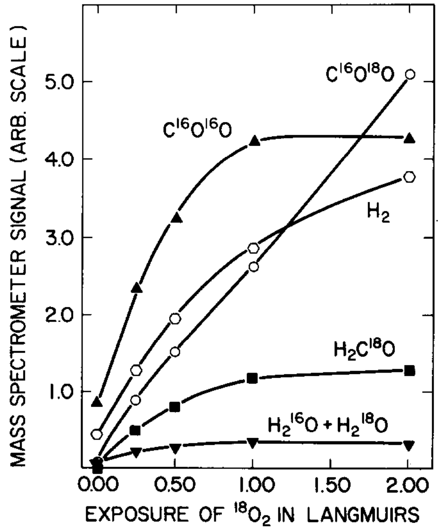


Fig. 5. The influence of oxygen exposure upon the production of the various oxidation products following a 100 sec exposure of $H_2C^{16}O$ at 180 K. The Cu(110) surface was always oxidized at 295 ± 10 K. These curves are uncirrected for detection sensitivities.

released in the exchange process ($H_2C^{16}O_{(a)} + {}^{18}O_{(a)} \rightarrow H_2C^{18}O_{(a)} + {}^{16}O_{(a)}$) subsequently oxidized another $H_2C^{16}O$ molecule to form the formate $HC^{16}O^{16}O$.

The oxygen variation study also showed that for oxygen-18 exposures less than ~1.6 L, corresponding to about 14% of a surface oxygen monolayer, more $C^{16}O^{16}O$ was produced than $C^{16}O^{18}O$. At these low surface concentrations of oxygen most of the ^{18}O atoms were evidently consumed in the exchange reaction with $H_2C^{16}O$. Only at higher exposures of oxygen, greater than ~1.6 L were there excess ^{18}O atoms on the Cu(110) surface to form more $C^{16}O^{18}O$ than $C^{16}O^{16}O$. Note that the production of $C^{16}O^{18}O$ increases linearly as a function of oxygen exposure, but the $C^{16}O^{16}O$ did not.

In the absence of surface oxygen only a small percentage of the $H_2C_{16}O$ molecules dissociated on the Cu(110) surface and the weakly bound $H_2C^{16}O$ desorbed below room temperature, see table 1. The adsorption of background oxygen may have contributed to the slight activity of the Cu(110) surface not intentionally exposed to $^{18}O_2$. Surface oxygen also enhanced the amount of $H_2C^{16}O$ that desorbed during the flash, but the increase was only marginal and not as dramatic as monitored for the oxidation products.

4. Discussion

The following observations were made in the preceding sections on the oxidation of $H_2C^{16}O$ on the Cu(110) surface:

(1) The magnitudes of the various product signals increased dramatically with increasing oxygen exposure.

(2) $H_2C^{16}O$ exchanged its oxygen-16 with surface ^{18}O atoms to give $H_2C^{18}O$.

(3) The ratio of $H_2C^{18}O/C^{16}O^{16}O$ was approximately unity.

(4) The $H_2(\delta)$, $C^{16}O^{18}O$, and $C^{16}O^{16}O$ peaks at ~470 K resulted from the decomposition of $HC^{16}O^{18}O$ and $HC^{16}O^{16}O$.

(5) The ratio of the $H_2(\gamma)/H_2(\delta)$ peaks was approximately unity.

(6) The $H_2(\gamma)/H_2C^{16}O$ peak was desorption limited.

The above observations suggested the following mechanism for the oxidation of $H_2C^{16}O$ on the Cu(110) surface:

$$H_2C^{16}O_{(g)} \rightarrow H_2C^{16}O_{(a)}\,, \tag{1}$$

$$H_2C^{16}O_{(g)} + {}^{18}O_{(a)} \rightarrow H_2C^{18}O_{(a)} + {}^{16}O_{(a)}\,, \tag{2}$$

$$H_2C^{16}O_{(g)} + {}^{16}O_{(a)} \rightarrow H_2C^{16}O^{16}O_{(a)}\,, \tag{3a}$$

$$H_2C^{16}O_{(g)} + {}^{18}O_{(a)} \rightarrow H_2C^{16}O^{18}O_{(a)}\,, \tag{3b}$$

$$H_2C^{16}O_{(a)} \rightarrow H_2C^{16}O_{(g)}\,, \tag{4a}$$

$$H_2C^{18}O_{(a)} \rightarrow H_2C^{18}O_{(g)}\,, \tag{4b}$$

$$H_2C^{16}O^{16}O_{(a)} \rightarrow H_{(a)} + HC^{16}O^{16}O_{(a)}\,, \tag{5a}$$

$$H_2C^{16}O^{18}O_{(a)} \rightarrow H_{(a)} + HC^{16}O^{18}O_{(a)}\,, \tag{5b}$$

$$2\,H_{(a)} + {}^{16}O_{(a)} \rightarrow H_2{}^{16}O_{(g)}\,, \tag{6a}$$

$$2\,H_{(a)} + {}^{18}O_{(a)} \rightarrow H_2{}^{18}O_{(g)}\,, \tag{6b}$$

$$H_{(a)} + H_{(a)} \rightarrow H_2(g) \quad \{\gamma\}\,, \tag{7}$$

$$HC^{16}O^{16}O_{(a)} \rightarrow H_{(a)} + C^{16}O^{16}O_{(g)}\,, \tag{8a}$$

$$HC^{16}O^{18}O_{(a)} \rightarrow H_{(a)} + C^{16}O^{18}O_{(g)}\,, \tag{8b}$$

$$H_{(a)} + H_{(a)} \rightarrow H_2(g) \quad \{\delta\}\,. \tag{9}$$

Some formaldehyde molecules also decomposed upon adsorption to form surface carbon, but this reaction pathway occurred only to a minor extent since the carbon buildup was negligible.

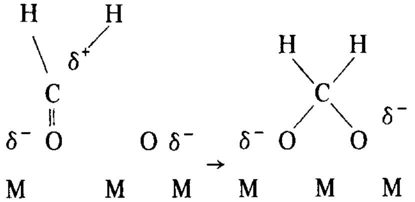
There was no experimental evidence to suggest that the intermediate HCO formed during the oxidation of H_2CO on Cu(100). Such an intermediate would be expected to yield some CO yet CO was not observed as a reaction product. The formation of HCO upon adsorption would have produced a substantial amount of water, but only trace amounts of water were observed since H_2CO was oxidized to H_2COO. Lastly, almost all of the formaldehyde adsorbed nondissociatively on an oxygen-free Cu(110) surface demonstrating that the clean copper surface was incapable of breaking the formaldehyde H–C bonds at low temperatures to produce HCO. The only surface intermediate that could account for the observed spectra was H_2COO.

The above mechanism for the oxidation of $H_2C^{16}O$ on Cu(110) was presented in a chronological sequence and represents the steps that were responsible for the observed products. Steps (1) to (3) occurred during the adsorption process. $H_2C^{16}O$ exchanged its oxygen with surface ^{18}O during adsorption, since both $H_2C^{16}O$ and $H_2C^{18}O$ exhibited the same desorption behavior as the sample was heated. It was highly unlikely that the H_2COO intermediate decomposed to HCOO during the adsorption process, because if HCOO were formed upon adsorption of H_2CO the H atoms released in this step would have reacted with nearby surface oxygen atoms to form water. In fact onyl small amounts of water were recorded at ~260 K indicating that H_2COO dissociated at this temperature after almost all of the oxygen atoms were consumed in steps (2) and (3). Furthermore, is step (5) had occurred upon adsorption, the H_2 peak would have been displaced well below 336 K, as was observed for D_2/HCOOD on this surface. The formation of $H_2C^{18}O$ from $H_2C^{16}O$ and $^{18}O_{(a)}$ also proceeded via such an intermediate. The intermediates formed upon adsorption therefore determined the product distribution observed at higher temperatures.

The formate has also been observed to be a very stable surface intermediate in reactions other than the decomposition of HCOOH and the oxidation of H_2CO.

The oxidation of CH_3OH on Cu(110) and Ag(110) single crystal surfaces demonstrated that a portion of the adsorbed CH_3OH was directly oxidized to a formate intermediate below room temperature [3,4]. In other adsorption studies on copper oxide catalysts in which more complex molecules were utilized, i.e., propylene, the existence of formate intermediate was also reported [5]. Blyholder [6] found that formate was stable on Ni, Fe, and CO surfaces and only disappeared when the metals were heated to 150–200°C in a background of H_2. Blyholder postulates that formate-type surface intermediates may be important in the Fischer–Tropsch synthesis, since he readily formed carboxylate structures from C_2H_4, CO, and H_2 mixtures.

The strong tendency for H_2CO to be oxidized to HCOO is readily understood once in the molecular bonding of H_2CO is examined. The carbonyl carbon is joined to three other atoms by σ bonds, and since these bonds utilize sp^2 orbitals, they lie in a plane 120° apart. The remaining p orbital of the carbon overlaps a p orbital of oxygen to form a π bond. The mobile π bond is pulled towards the more electronegative oxygen atom, and hence the electrons of the carbonyl double bond are not equally shared. The carbon atom in the H_2CO molecule thus can be an electron acceptor (eletrophile) and will react with other species that are electron donors (nucleophiles), such as adsorbed atomic oxygen. The oxidation of H_2CO to HCOO can also be viewed in the much broader context of Lewis acid-base reactions, in which adsorbed oxygen acts as a Lewis base and interacts strongly with the acidic carbon in the adsorbed H_2CO. Recent theoretical calculations indicate that H_2CO bonds to metal surfaces via the oxygen lone pairs through an electrostatic interaction [7]. The reaction to form $H_2COO_{(a)}$ can then be envisioned as



The adsorption/desorption kinetics of hydrogen from copper single crystal surfaces was recently studied with molecular beams by monitoring the catalytic exchange of H_2 with adsorbed deuterium atoms on the (100), (110), and (310) of copper [8]. Balooch et al. showed that the dissociative adsorption of hydrogen on copper proceeded with a translational energy activation barrier perpendicular to the surface. The desorption of HD from the copper surfaces exhibited angular distributions that were nondiffuse, in excellent agreement with angular distributions observed in permeation experiments of hydrogen through bulk copper crystals. In view of these observations, Cardillo et al. suggested that the principle of detailed balancing (microscopic reversibility) may be of general applicability to gas–solid interactions [9]. They concluded that since the copper surface selectively removed the "hotter" hydrogen molecules from the gas phase (because of the activation barrier for H_2 adsorption) the copper surface would have to return to the gas phase a distribution of H_2 molecules that were translationally hot to maintain an equilibrium distribution far from the surface. Palmer et al. originally suggested that the non-diffusive desorption of HD may be due to a stringent requirement on the trajectories of the colliding partners; requiring them to be colliding with an appreciable normal momentum component [10]. The extremely low frequency factor calculated in the present work for the desorption of deuterium from Cu(110), $\sim 1 \times 10^{-7\pm1}$ cm^2/sec, suggested that only a very small fraction of the deuterium atoms that collided on the copper surface satisfied the stringent requirements necessary for desorption as D_2, because frequency factors for two dimensional reactions without entropy barriers would typically be expected to be 10^{-1}–10^{-3} cm^2/sec [11]. For this system (H_2/Cu) the principle of microscopic reversibility seems to hold, as there are severe "steric" hindrances for the second order recombination and desorption of H_2. In terms of statistical mechanics this steric hindrance means that only a small volume of phase space accessible to the colliding partners actually produces a stably recombined atom pair which can leave the surface. This implies that there are strict geometric constraints on the collision trajectory (or transition state) for the recombination reaction. Similar conclusions have been reached by Gelb and Cardillo, who have calculated the potential energy surface for the dissociative *adsorption* [12–14].

Acknowledgements

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Appendix

The fragmentation patterns of $H_2C^{18}O$ and CH_3OH are presented in table 2 [15]. Both cracking patterns are quantitatively indistinguishable except for the $m/e = 15$ (CH_3^+) signal present for CH_3OH. The absence of an $m/e = 15$ signal below room temperature demonstrated that only $H_2C^{18}O$ desorbed below room temperature when $m/e = 32$ was monitored; a small $m/e = 15$ signal persisted at $T \sim 360$ K. When $^{16}O_2$ was substituted for $^{18}O_2$ it was found that this peak was due to CH_3OH. Previous work on the oxidation of methanol on Cu(110) showed that a methoxide intermediate was formed and dissociated at ~360 K to yield H_2CO, H_2, and CH_3OH [3]. The small formaldehyde and methanol peaks observed at ~360 K in this study were thus attributed to the methanol impurity present in

Table 2
Fragmentation patterns

	m/e	Identity	Abundance
CH_3OH	31	CH_2OH	100
	32	CH_3OH	80
	29	CHO	33
	15	CH_3	10
	30	CH_2O	5.2
$H_2C^{16}O$	29	$HC^{16}O$	100
	30	$H_2C^{16}O$	88
	28	$C^{16}O$	30
$H_2C^{18}O$	31	$HC^{18}O$	100
	32	$H_2C^{18}O$	88
	30	$C^{18}O$	30

the formaldehyde vapor. These CH_3OH and $H_2C^{16}O$ signals were removed from the figures shown in this paper.

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