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Decomposition of Formic Acid on Copper, Nickel, and Copper–Nickel Alloys

II. Catalytic and Temperature-Programmed Decomposition of Formic Acid on Cu/SiO_2, Cu/Al_2O_3, and Cu Powder

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Turnover rates for the catalytic dehydrogenation of formic acid (HCOOH) on Cu/SiO_2, Cu/Al_2O_3, and Cu powder between 380 and 500K are reported. The turnover rate is independent of HCOOH partial pressure between 1.5 and 6 kPa, concentration of decomposition products, metal loading (0.33–19.2%), metal dispersion (0.03–22%), and the nature of the support. HCOOH adsorption on Cu at room temperature leads to the formation of surface formate. Its decomposition rate constant agrees with that reported for the catalytic decomposition of HCOOH on Cu, and the decomposition of HCOOH preadsorbed on Cu(110) at low coverage.

INTRODUCTION

The catalytic decomposition of gas-phase HCOOH has been widely used to test the catalytic properties of metals, alloys, and oxides (*1–4*). On Cu, infrared (*5*), kinetic isotope effect (*6*), and decomposition rate (*7–24*) measurements have yielded some information on the reaction mechanism. Formate is apparently the most abundant surface species following chemisorption and subsequent removal of gas-phase HCOOH (*5*), but adsorbed HCOOH is also observed in the presence of gaseous acid (*5*) and during its catalytic decomposition on Cu (*7*). The decomposition of HCOOH preadsorbed at low surface density on Cu(110) (*25*) and polycrystalline Cu films (*26*) was studied to demonstrate the use of temperature-programmed desorption (TPD) in the measurement of surface reaction rate constants. The products were formed from the decomposition of surface formate (*25–27*). In the present study, the conditions under which the subsequent step, the application of surface reaction rate constants to the corresponding step in a catalytic sequence, may be taken are considered. Zero-order HCOOH decomposition rate constants, corresponding to the decomposition of the most abundant surface intermediate on Cu/SiO_2, Cu/Al_2O_3, and Cu powders of known metal surface area, are reported.

EXPERIMENTAL

Catalyst Preparation and Characterization

The preparation and characterization of the catalysts used in this study are described in detail elsewhere (*28*). The Cu dispersion was calculated from N_2 physisorption, oxygen uptake during N_2O decomposition, and X-ray line-broadening, as described elsewhere (*28*).

Bulk Cu formate was prepared by adding Cu carbonate (Baker Analyzed Reagent) to an aqueous solution (3 *N*) of HCOOH (Aldrich) at room temperature (*31*). Copper formate was precipitated from solution by evaporation at 363K. The X-ray diffraction

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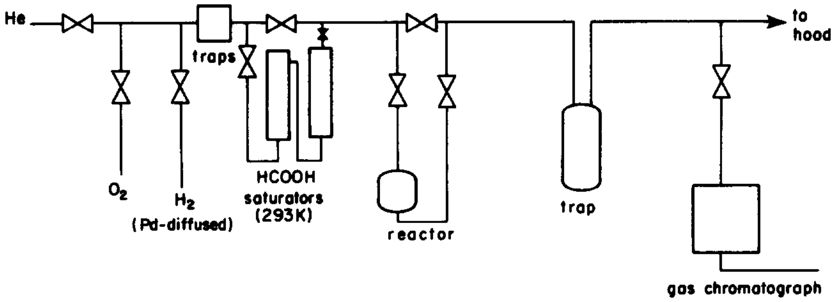

FIG. 1. Schematic diagram of apparatus.

pattern was identical to that reported for anhydrous cupric formate (*32*). The Cu, H, and C weight fractions, measured by atomic absorption and combustion analysis, were 0.410, 0.0132, and 0.156, respectively, very similar to those predicted for anhydrous cupric formate (0.414, 0.0130, and 0.156).

Apparatus and Procedure

Catalytic experiments. Dehydrogenation turnover rates and related parameters were measured in the flow apparatus described schematically in Fig. 1. Prereduced and passivated catalysts (surface area 0.2–0.5 m^2) were charged into the reactor; powders were mixed with ground quartz (20–30 wt% metal). The catalysts were rereduced in flowing Pd-diffused H_2 ($\nu_{H_2}{}^s = 4\text{–}10\ s^{-1}$)[1] for 2 h. Supported catalysts were reduced at 493K and powders at 723K. Following reduction, the samples were cooled in He to the reaction temperature and the He stream was routed through the HCOOH saturator.

Helium was purified by passage through a trap containing Cu/SiO_2 (35 wt% Cu) at 523K, and another trap containing molecular sieve (5A, Linde) cooled by liquid nitrogen. Purified He was allowed to contact liquid HCOOH in a two-stage saturator maintained at constant temperature (283–293K) by recirculating an ethylene glycol–water mixture. HCOOH (3–5% water, Aldrich) was purified by fractional crystallization, vacuum distillation, and outgassing, as described elsewhere (*33*). The effective pressure of HCOOH monomer could be varied between 1.5 and 6 kPa. The HCOOH-saturated gas was passed through a preheating section in the reactor and allowed to contact the catalyst. The concentration of the decomposition products (CO_2, CO, H_2) was measured by gas chromatography using a Porapak-Q column at 343K, He or Ar carrier gas, and a thermal conductivity detector. Unreacted HCOOH and any water formed were condensed after the reactor in a Pyrex coil cooled by a dry ice–acetone bath.

The fractional HCOOH conversion (X_F) was calculated from the concentration of products in the carrier gas at reactor temperatures between 380 and 500K. The dehydrogenation turnover rate (N), defined as the average number of H_2 or CO_2 molecules formed per unit time per surface Cu atom, was calculated from

$$N\,(s^{-1}) = \nu_F{}^s X_F, \qquad (1)$$

where $\nu_F{}^s$ is the HCOOH site-contact frequency. Typical values of X_F and $\nu_F{}^s$ were 0.001–0.5 and 0.1–6.0 s^{-1}, respectively.

The effects of temperature, HCOOH conversion, and concentration of reactants or products in the carrier gas on the turnover rate were examined. The activation energy and preexponential factor were determined from the temperature dependence of the rate, measured at rising and falling

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[1] The quantity $\nu_{H_2}{}^s$ is defined as the number of dihydrogen molecules entering the reactor for unit time per surface metal atom determined from gas uptake measurements before reaction; it represents a site-contact frequency.

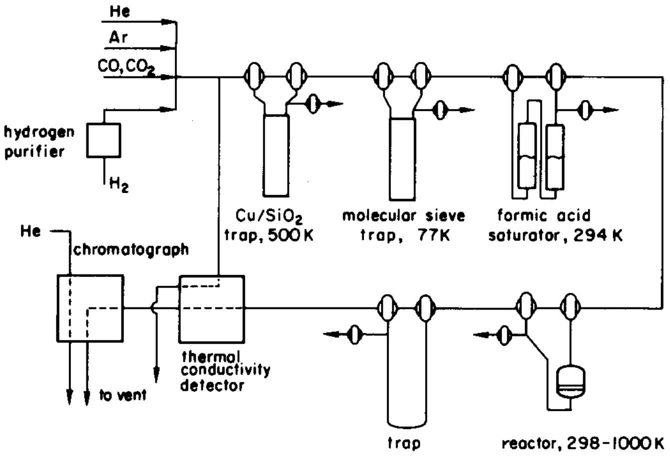


FIG. 2. Schematic diagram of temperature-programmed reaction apparatus.

temperature to rule out hysteresis or deactivation.

Temperature-programmed decomposition apparatus and procedure. The decomposition of HCOOH preadsorbed on Cu was measured in the Pyrex flow apparatus described schematically in Fig. 2. The gases were purified by passage through a catalytic H_2 purifier (Deoxo Pd catalyst, Engelhard) and traps containing Cu/SiO_2 at 500K and 5A molecular sieve cooled by dry ice or liquid nitrogen. The purification of HCOOH and the saturation of the carrier gas were carried out as previously described. HCOOH pressure in the carrier gas was varied between 5 and 7 kPa.

Copper powder and Cu/SiO_2 (metal surface area 3–8 m^2) were placed on a porous quartz frit inside a vertically mounted quartz reactor. The reactor was resistively heated. The temperature was measured by a Chromel–Alumel thermocouple placed inside a thin glass sheath in contact with the sample. The temperature could be raised linearly between 300 and 1200K at rates (β) between 0 and 0.5K s^{-1}.

The total concentration of decomposition products in the carrier gas was measured by a thermal conductivity detector (Perkin–Elmer Sorptometer 212C). The various products were separated by gas chromatography (Aerograph, 31-012, Porapak-Q, 303K, thermal conductivity detector), by partial condensation of the decomposition products, or by changing the carrier gas (He, Ar). A trap cooled by dry ice–acetone was used to condense any water or HCOOH leaving the reactor during reduction, preadsorption, and decomposition experiments.

The rate of product evolution during TPD is proportional to the concentration of products in the carrier gas. These were calculated from thermal conductivity measurements and plotted as a function of sample temperature. The latter was adjusted for any time delay between desorption and detection. Evolution rate data were integrated to obtain the surface density of adsorbed species.

A prereduced and passivated copper powder sample, Cu(B) (8 g), was reduced in flowing H_2 (20% H_2–Ar, $\nu_{H_2}{}^s = 1.0$ s^{-1}) by raising the temperature from 300 to 673K at a rate of 0.09K s^{-1}. The area under the H_2 consumption peaks corresponded to two monolayers of CuO at the surface. The sample was cooled to room temperature in flowing He and flushed until the H_2 concentration was less than 0.01%. The He stream was routed through the saturators; the sample was exposed to the acid-saturated carrier ($\nu_F{}^s = 0.025$ s^{-1}, 6 kPa HCOOH) for 600 s. The saturators were then bypassed, and the sample was flushed with He or Ar ($\nu^s = 0.6\ s^{-1}$) at room temperature for 600–1800 s. The carrier flow rate was decreased ($\nu^s = 0.1$–$0.2\ s^{-1}$) and the temperature was increased linearly from 300 to 573K at the rate of 0.09K s^{-1}.

Prereduced and passivated SiO_2-supported Cu (Cu(35)/SiO_2, 1.2 g) was rereduced in flowing H_2 (20% H_2–Ar, $\nu_{H_2}{}^s = 0.2\ s^{-1}$). The reduced sample was cooled in He to room temperature and exposed to HCOOH ($\nu_F{}^s = 0.05\ s^{-1}$, 6 kPa HCOOH, 0.7 ks). It was then flushed with carrier gas ($\nu^s = 0.6\ s^{-1}$, 1.8 ks) to remove any physisorbed acid. The temperature of the sample was raised linearly from 300 to 773K at 0.18K s^{-1}.

The temperature-programmed decomposition of bulk Cu formate was measured in the apparatus described in Fig. 2. Formate powder (0.004–1.4 g) was mixed with ground quartz (0–93 wt% quartz) and placed in the reactor. The temperature was raised linearly from 300 to 673K at 0.045K s^{-1} in flowing He.

RESULTS

Catalytic Decomposition of Formic Acid

The decomposition turnover rate on all Cu catalysts is independent of HCOOH pressure (2–6 kPa), site-contact frequency (0.1–6.0 s^{-1}), and fractional conversion (10^{-4}–0.5), and of the pressure of CO, CO_2, and H_2 (0–8 kPa) in the carrier gas. HCOOH dehydration does not occur on Cu. Measurements of the decomposition rate on alumina and ground quartz show that traces of dehydration products (CO and H_2O) observed during the reaction on Cu arose from the decomposition of HCOOH on the support or the diluent.

The activation energy and preexponential factor for the catalytic dehydrogenation of HCOOH on Cu were determined from Arrhenius plots of the turnover rate. The results are shown in Table 1.

TABLE 1

Activation Energy and Preexponential Factor for the Zero-Order Catalytic Dehydrogenation of HCOOH on Cu

Catalyst	Cu fractional dispersion[a]	E (kJ mol^{-1})	log A (s^{-1})	T_0[b] (K)
Cu(0.33)/Al_2O_3[c]	0.054	97.0	10.15	463
Cu(1.0)/Al_2O_3	0.074	98.5	10.55	455
Cu(1.7)/Al_2O_3	0.148	97.5	10.40	455
Cu(2.3)/Al_2O_3	0.218	100.0	10.55	460
Cu(3.1)/Al_2O_3	0.084	97.0	10.35	455
Cu(4.8)/Al_2O_3	0.082	98.0	10.45	456
Cu(7.2)/Al_2O_3	0.035	94.5	10.05	455
Cu(9.6)/Al_2O_3	0.028	99.5	10.70	453
Cu(12.0)/Al_2O_3	0.043	97.0	10.30	457
Cu(14.4)/Al_2O_3	0.045	94.0	9.90	460
Cu(19.2)/Al_2O_3	0.031	96.0	10.2	456
γ-Al_2O_3	—	90.5 (108.0, dehydration)	4.75 (7.05, dehydration)	—
Cu(35)/SiO_2	0.040	97.0	10.40	450
Cu	0.0011	96.5	9.80	472
Cu(A)	0.0004	95.0	9.85	465
Cu(C)	0.003	99.5	10.00	480

[a] Ratio of surface to bulk Cu atoms, measured from oxygen uptake during N_2O decomposition (*28*).

[b] Isokinetic temperature, temperature at which the zero-order turnover rate reaches 0.16 s^{-1}.

[c] Preparation described elsewhere; Cu(X)/Y, Cu supported on Y with X wt% metal loading.

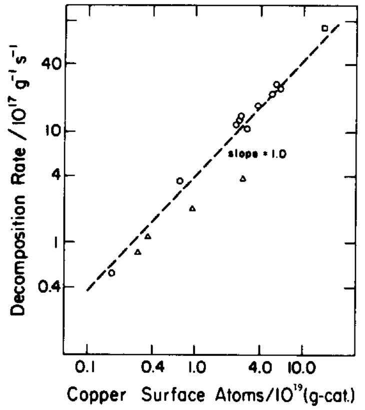


FIG. 3. Koros–Nowak test. HCOOH dehydrogenation on Cu (435K). △, Cu; ○, Cu/Al_2O_3; □, Cu/SiO_2.

The activation energy is almost identical on all Cu catalysts (94.5–100 kJ mol^{-1}); it is independent of Cu loading (0.33–35 wt%) and dispersion (0.04–22%), and of the nature of the support. The isokinetic temperature, defined as the temperature at which a given value (0.16 s^{-1}) of turnover rate is measured, is similar for all supported catalysts, but slightly higher on Cu powder (Table 1).

The absence of mass and heat transfer limitations, catalysis by the support, and poor reactant–catalyst contacting was demonstrated by the successful application of the Koros–Nowak criterion (*34, 35*). This test, as applied to supported metals, involves the measurement of reaction rates on a series of samples with varying metal loading but similar dispersion. In the absence of artifacts, the reaction rate is proportional to the number of surface metal atoms. The slope of unity in the logarithmic plot shown in Fig. 3 demonstrates that the rate is that of the surface-catalyzed reaction, unaffected by transport processes or other artifacts. The conclusion holds throughout the experimental temperature range because the activation energy is identical on all Cu catalysts.

The decomposition of HCOOH at 488K on Cu powder preoxidized by exposure to air at 373K resulted in its reduction. The turnover rate increased with time but reached steady state in less than 0.2 h; the steady-state rate is identical to the value before O_2 exposure. Above 505K, the dehydrogenation rate on reduced Cu powder increased steadily (30–60%) over 1 h, but remained constant thereafter. The turnover rates reported in this study were measured below this temperature.

Temperature-Programmed Decomposition of Preadsorbed Formic Acid

The rate of evolution of CO_2 and H_2 during the decomposition of HCOOH preadsorbed at room temperature on Cu powder (Cu(B)) is shown in Fig. 4. Each desorption rate–temperature curve corresponds to an adsorption–decomposition experiment without rereduction between experiments. Dihydrogen is evolved during HCOOH preadsorption at room temperature; the amount could not be determined accurately, but it is approximately equal (±30%) to the amount of H_2 evolved during TPD.

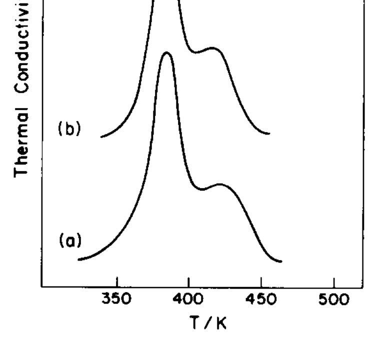
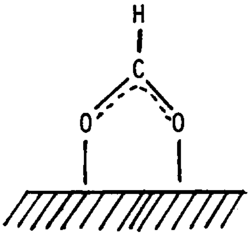


FIG. 4. Temperature-programmed decomposition of HCOOH preadsorbed on Cu powder (β = 0.09K s^{-1}, $\nu^{s}_{carrier}$ = 0.1 s^{-1}). (a) CO_2/HCOOH (300K); (b) CO_2/HCOOH (300K); (c) H_2/HCOOH (300K).

CO_2 and H_2 evolution peaks are identical. Peaks at 386 ± 3 and 422 ± 4K are observed for both products; it is possible that a third peak occurs between these two. The ratio of CO_2 to H_2 evolved is 1.9 ± 0.2, as in formate ions:



(2)

The ratio of CO_2 molecules evolved to surface Cu atoms, measured from N_2 physisorption between experiments, assuming a surface density of Cu atoms equal to 1.6×10^{15} cm^{-2}, is 0.25 ± 0.05. This suggests that only a fraction of the Cu surface adsorbs HCOOH irreversibly at room temperature, or that it takes four adjacent Cu surface atoms to form surface formate species. CO was not detected in the decomposition products.

No measurable desorption (<0.02 monolayer) was observed following exposure of Cu powder to H_2 (22 kPa) and CO_2 (1 kPa) at room temperature. Therefore, the rate of evolution of CO_2 and H_2 during TPD was determined by the decomposition rate of adsorbed formate. No H_2 consumption was detected during temperature-programmed reduction (TPR) of the samples (to 773K) in flowing H_2 after several adsorption–decomposition cycles or catalytic decomposition ($\nu_F{}^s = 0.03$ s^{-1}) at 523K for 0.3 h. Therefore, no strongly held species remained at the surface after these experiments.

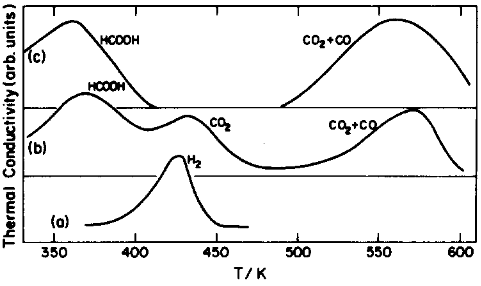


FIG. 5. Temperature-programmed decomposition of HCOOH preadsorbed on $Cu(35)/SiO_2$. (a) H_2/HCOOH (300K); (b) CO_2, CO, HCOOH/HCOOH (300K); (c) CO_2, CO, HCOOH/HCOOH (300K), blank SiO_2.

The results of TPD of HCOOH preadsorbed on $Cu(35)/SiO_2$ are shown in Fig. 5. Evolved HCOOH was measured from the concentration of the products of its decomposition (CO_2, H_2) on a Cu powder trap placed after the reactor. Comparison of the top two curves shows that the low-temperature peak corresponds to desorption of unreacted HCOOH from SiO_2, while the high-temperature peak consists of CO_2 and CO resulting from the decomposition of HCOOH preadsorbed on SiO_2. The CO_2 peak at intermediate temperature arises from the dehydrogenation of HCOOH preadsorbed on Cu. It coincides with the H_2 evolution peak (Fig. 5a) observed when Ar was used as the carrier gas. The ratio of CO_2 to H_2 evolved is 1.8 ± 0.5, as in formate ions. The ratio of CO_2 evolved to Cu surface atoms is 0.6 ± 0.2; the number of surface atoms was estimated from the metal surface area measured by oxygen uptake measurements (*28*) before TPD experiments. Again, no adsorbed species remained at the surface following HCOOH adsorption–decomposition or catalytic experiments.

Temperature-Programmed Decomposition of Bulk Copper Formate

CO_2 and H_2 were the only products of the decomposition of bulk Cu formate. CO_2 was evolved in two peaks, at 460 and 475K, during TPD experiments ($\beta = 0.045K$ s^{-1}). The ratios of CO_2 and H_2 molecules to Cu atoms in the starting material were 2.0 ± 0.2 and 0.9 ± 0.1, respectively. Therefore, if HCOOH was formed during the decomposition of Cu formate, it decomposed to CO_2 and H_2 on the Cu residue before leaving the reactor. A metallic mirror was observed on the reactor walls following the decomposition; it was previously attributed to the formation and subsequent decomposition of a

TABLE 2

Zero-Order Catalytic Dehydrogenation of HCOOH on Cu. Summary of Literature Data

Catalyst type	A^a (s^{-1})	E (kJ mol^{-1})	$T_0{}^b$ (K)	T (K)	P (kPa)	Ref.
Powder	8×10^{12}	113	431	338–372	1.33	*7*
Cu{111}	—	99.5	—	455–525	5.33	*8*
Cu{110}	—	97	—	455–525	5.33	*8*
Film	—	98	—	455–525	5.33	*8*
Powder	—	53–81	—	373–433	5.33	*9*
Foil	—	93	—	393–473	—	*10*
Foil	—	100.5–104.5	—	~620	101.3	*11*
Powder	2×10^{15}	122.5	395	319–354	3.2	*6*
Film	5×10^{11}	111	463	373–573	3.2	*12*
Foil	5×10^{13}	150.5	521	523–573	101.3	*13*
Powder	1×10^{7}	85	570	353–473	1.3–3.3	*14*
Film	—	78	—	~473	4.8	*15*
Foil	—	113	—	540–625	101.3	*16*
Wire	—	113–130	—	540–625	101.3	*16*
Cu/ZnO	—	61.5	—	403–433	101.3	*17*
Wire	—	95.5	—	460–650	101.3	*18*
Foil	—	98	—	~453	3.3	*19*
Foil	—	93	—	393–513	4.7	*20*
Foil	—	102.5	—	473–573	101.3	*21*
Foil	—	100	—	~620	101.3	*22*
Cu/Al_2O_3	—	80.7	—	403–453	101.3	*23*
Film	—	90.3	—		10^{-4}–10^{-3}	*24*

[a] Per surface copper atom, assuming a surface density of 1.5×10^{15} cm^{-2}; reported only for those studies where copper surface area measurements were reported.

[b] Temperature at which a turnover rate of 0.16 s^{-1} is measured.

volatile, unstable Cu(I) formate intermediate (*36–38*). The product evolution peaks are not affected by changing the carrier flow rate, and therefore, the concentration of the products during the reaction. The decomposition peaks are narrow, characteristic of autocatalytic reactions, as previously reported (*36–38*). Autocatalysis results from the nucleation and growth of Cu metal nuclei, with the decomposition reaction occurring at the metal–metal formate interface. Indeed, the decomposition of bulk Cu formate occurs at higher temperature than the decomposition of preadsorbed HCOOH, apparently because of the delay associated with the nucleation step. Dilution of Cu formate with ground quartz led to an increase in the decomposition temperature. X-Ray diffraction of the residue shows that it is metallic Cu.

DISCUSSION

Catalytic Decomposition

The activation energy and product composition of the catalytic decomposition of HCOOH on Cu agree with most values previously reported in the literature (Table 2). Few of these studies reported measurements of the Cu surface area, preventing the calculation of turnover rates. Turnover rates on supported Cu catalysts were never reported before this study. The reported isokinetic temperature on Cu powders, films, and foils is between 395 and 570K, corresponding to a factor of 10^3 difference in turnover rate. In this study, the isokinetic temperature is between 450 and 477K on all catalysts. The turnover rate is four times greater on supported than on unsupported Cu, but the activation energy is identical.

The insensitivity of turnover rate to particle size (5–40 nm) and to the nature of the support suggests that the catalytic decomposition of HCOOH on Cu is structure insensitive. The results agree with previous reports of similar decomposition activation energy on preferentially oriented and polycrystalline Cu (Table 2).

The successful application of the Koros–Nowak criterion demonstrates that the measured turnover rate and activation energy correspond to the surface-catalyzed decomposition steps. Lower values of these, reported in the literature, may have been affected by rate-limiting physical transport processes.

Carbon dioxide and dihydrogen are primary products of the decomposition reaction; they are not formed from dehydration products by the water-gas shift reaction, because the ratio of CO_2 to CO is greater than that predicted from the equilibrium constant of this reaction.

Temperature-Programmed Decomposition

The composition of TPD products and the evolution of H_2 during HCOOH preadsorption on Cu suggest the presence of formate species irreversibly adsorbed on Cu at room temperature. The shape of the product evolution peaks suggests that the decomposition rate is proportional to the surface density of formate. The rate constant was calculated in two ways:

(i) a preexponential factor of 10^{13} s^{-1} was assumed and the activation energy was calculated from the peak temperature (T_p) using (*39, 40*)

$$(E/RT_p^2) = (\nu/\beta)\exp(-E/RT_p); \quad (3)$$

(ii) the activation energy was calculated from the peak width at half-maximum ($\Delta T_{1/2}$) using (*41*)

$$(E/RT_p) = 2.466[1 - 0.5725(T_p/\Delta T_{1/2})]; \quad (4)$$

the preexponential factor was then calculated from Eq. (3).

The kinetic parameters obtained from the two methods are shown in Table 3. Rate constants calculated from catalytic data, and from previously reported TPD of HCOOH adsorbed on Cu(110) and Cu films at low pressure, are also shown in Table 3. The peak shapes calculated from the rate constants (method (ii)) are identical to those found experimentally.

H_2 and CO_2 are apparently formed in the same decomposition step. The activation energy corresponding to the two peaks of each product observed during TPD of HCOOH adsorbed on Cu powder differs by 10 kJ mol^{-1}. Only the higher activation energy peak was observed on Cu/SiO_2. The multiple peaks may arise from decomposition of HCOOH adsorbed on differently oriented surface regions of a polycrystalline powder. Smaller Cu crystallites may show preferential orientation, and predominance of one or two low-index planes at the surface.

The agreement between the rate constants calculated in this study and those obtained by other authors on Cu(110) under ultrahigh-vacuum conditions is excellent (*25*) (Table 3). The formate surface density (10^{18} m^{-2}) and HCOOH exposure (10^{-3} Pa-s) were lower than those in this study (10^6–10^7 Pa-s, 4×10^{18} m^{-2}). The decomposition products and the composition of the adsorbed species are identical in both studies. As in the decomposition of bulk Cu formate and the catalytic decomposition of HCOOH, only dehydrogenation products are observed.

Comparison of Catalytic and TPD Data

The translation of surface reaction rate constants into those of the corresponding step in a catalytic sequence requires that the identity and decomposition rate constant of the adsorbed species do not change with surface density of reactive and coadsorbed species. The zero-order HCOOH decomposition turnover rate is given by

TABLE 3

Rate Constants Calculated from Temperature-Programmed Decomposition of HCOOH Preadsorbed on Cu

Sample	Product	Method (i)		Method (ii)		Isokinetic temperature (K) ($N = 0.16$ s^{-1})
		E (kJ mol^{-1})	A (s^{-1})	E (kJ mol^{-1})	A (s^{-1})	
Copper powder	$CO_2(\alpha)$/HCOOH(RT)	112	10^{13}	117	4×10^{13}	422
	$CO_2(\beta)$/HCOOH(RT)	123	10^{13}	—	—	463
	$H_2(\alpha)$/HCOOH(RT)	111	10^{13}	115	3×10^{13}	418
	$H_2(\beta)$/HCOOH(RT)	123	10^{13}	—	—	463
Silica-supported copper	CO_2/HCOOH(RT)	122	10^{13}	—	—	463
	H_2/HCOOH(RT)	122	10^{13}	133	6×10^{13}	463
Cu(110)	Ying and Madix (*25*), TPD			133	1×10^{14a}	467
Copper powder	This study, zero-order, catalytic decomposition			96.5	7×10^{9a}	470
				96.5	7×10^{10b}	430
Silica-supported copper				97	2×10^{10a}	454
				97	2×10^{11b}	417

[a] Assuming one adsorbed intermediate per surface Cu atom.

[b] Assuming only 0.1 of surface Cu atoms participate in the catalytic decomposition reaction.

$$N = k\theta_{\text{sat}} \quad (5)$$

for a unimolecular surface decomposition step. The rate constant (k) is the parameter available from TPD data; θ_{sat} is the ratio of adsorbed intermediate to surface metal atoms during the zero-order catalytic decomposition. An apparent decomposition rate constant may be calculated from turnover rate data by assuming a value for θ_{sat}. The isokinetic temperature (for $k = 0.16$ s^{-1}) is shown in Table 3 for catalytic and TPD data and two values of θ_{sat}. It has been shown (*33*) that the isokinetic temperature calculated from TPD rate constants is only dependent, to a first approximation, on the desorption peak temperature and not on the preexponential factor and activation energy chosen to describe the peak. The agreement among the data in Table 3 is reasonable. The range of isokinetic temperature (420–470K) corresponds to a difference of a factor of 20 to 30 between the highest and lowest values of the decomposition rate constant.

The activation energy for the catalytic HCOOH decomposition on Cu (97 kJ mol^{-1}) is lower than that for the decomposition of HCOOH preadsorbed on Cu (115–133 kJ mol^{-1}). The lower values may result from the role of physisorbed HCOOH, present at the surface during catalytic but not TPD experiments, on the decomposition step. A bimolecular mechanism, involving HCOOH–formate species as the most abundant surface intermediate, was proposed to explain the kinetic isotope effect measured for the decomposition of all deuterated acids on Cu (*6*), and the presence of large amounts of physisorbed acid on Cu during the catalytic reaction (*5*, *7*).

CONCLUSIONS

The turnover rate of the catalytic decomposition of HCOOH on Cu/SiO_2, Cu/Al_2O_3, and Cu powder is independent of HCOOH pressure, concentration of decomposition products, metal loading and dispersion, and the nature of the support. Only dehydrogenation products were observed during catalytic decomposition of HCOOH, TPD of HCOOH preadsorbed on Cu, and decomposition of bulk Cu formate. The rate constants calculated from the former two experiments are similar and agree with previous data on the decomposition of HCOOH preadsorbed at low surface density on Cu(110). This study demonstrates that rate constants calculated from TPD may be applied to the corresponding surface-catalyzed step in a catalytic sequence, provided the identity and decomposition mechanism of the adsorbed species are not affected by the surface density of coadsorbed species.

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