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Adsorption of Water on Polycrystalline Copper: Relevance to the Water Gas Shift Reaction

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This paper is concerned with the interaction of water with a polycrystalline copper surface. It shows that a small fraction (7–8%) of the copper surface will readily dissociatively chemisorb water, while the major portion of the surface adsorbs water in a molecular form [ΔH(ads) = 45 kJ mol^{-1}]. The structure sensitivity of the adsorption of water on the polycrystalline surface is shown to have a critical effect on the proclivity of copper to act as a catalyst for the water gas shift reaction. The mechanics of this process appear to involve oxidation of the copper surface (by water), followed by a facile surface reduction (by carbon monoxide) and subsequent regeneration of the active copper sites by recombinative desorption of atomic hydrogen. The activation energy of the reaction is 67–75 kJ in the range 350–400 K. The presence of adsorbed formate species on the copper catalyst is shown to be inconsequential to the progress of the water gas shift reaction.

1. INTRODUCTION

The low-temperature (573 K) conversion of carbon monoxide and steam to carbon dioxide and hydrogen is effected by the use of highly active copper–zinc oxide–alumina catalysts, although there is still considerable debate as to the nature of the active site on the catalyst surface and the mechanism of the reaction. It has been suggested (*1*) that a copper–zinc oxide couple is the seat of activity within these catalysts, while other workers (*2–4*) have reported evidence to suggest that the activity is determined exclusively by the copper surface.

An associative mechanism has been proposed (*1*, *5–7*) in which the formation and subsequent decomposition of a surface formate intermediate are considered to be the likely reaction route. Alternatively, several workers (*4*, *8–10*) have suggested that the reaction proceeds via a regenerative mechanism involving the sequential oxidation and reduction of the copper surface.

A number of UHV studies have shown that the adsorption of water does occur on copper single-crystal surfaces and that the adsorption is distinctly surface structure sensitive. Thus, on a Cu(100) surface only molecular adsorption appears to occur (*11*), whereas on both the Cu(111) and Cu(110) faces there is some tendency for surface hydroxylation (*12*) or even complete dissociation of the adsorbed water (*13*). Structure sensitivity of the adsorption is also claimed from a study of the adsorption and subsequent desorption of water on evaporated copper films (*14*). In this study it was claimed that "surface roughness in copper promotes decomposition of adsorbed water molecules." In sharp contrast to these claims both Bange *et al.* (*15*) and Clendening *et al.* (*16*) could find no evidence for the decomposition of water on ordered, but atomically rough, Cu(110) surfaces. Further to the recent observation (*8*) that adsorbed oxygen is produced by the interaction of steam with polycrystalline copper surfaces at 346 K, this study was undertaken in an attempt to characterize the adsorption and

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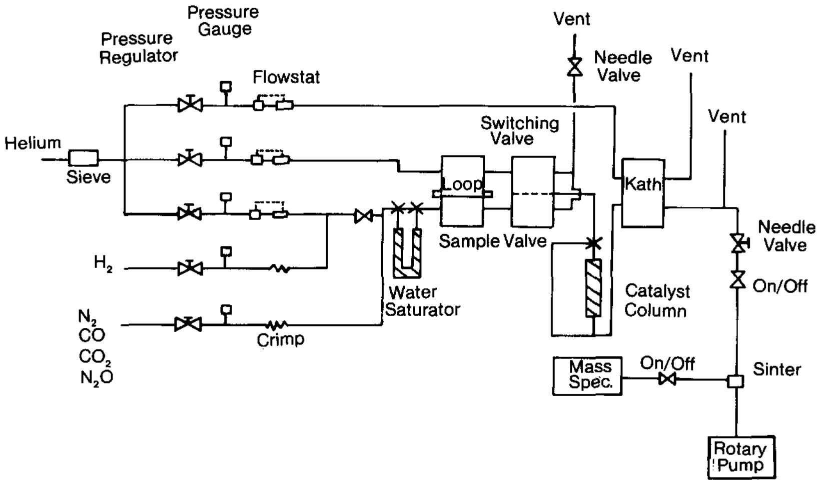

FIG. 1. Schematic representation of low-pressure flow microreactor apparatus.

reaction of water with reduced polycrystalline copper powders and to examine the relevance of these processes in the low-temperature water gas shift reaction.

2. EXPERIMENTAL

Apparatus

The apparatus, which permitted *in situ* surface area determinations, adsorption, temperature-programmed desorption (TPD), and temperature-programmed reaction (TPR), was similar to that described previously (*8*), except that a water saturator was added to permit the introduction of controlled amounts of water to the catalyst column. The apparatus is shown schematically in Fig. 1. The saturator consisted of a Pyrex glass U-tube packed with molecular sieve, which was moistened by injection of a small amount of distilled water. Passage of the helium carrier gas stream through the saturator produced an eluant containing ~1.5 vol% water vapor. The saturator was surrounded by an ice bath, resulting in a reduction in the water vapor content of the gas stream to ~0.5 vol%.

Materials

Helium (BOC Ltd) was purified by passage through a rare gas purifier (BOC Mk3) to reduce, to the parts per million level, traces of nitrogen, hydrogen, water, carbon dioxide, and hydrocarbons. The oxygen impurity level was estimated to be 0.116 ppm, which increased to 160 ppm on passage through the water saturator.

Hydrogen (Air Products Ltd, 99.99% purity); carbon monoxide (Matheson Inc. 99.99% purity), carbon dioxide (Distillers Co. Ltd, 99.965% purity), and nitrous oxide (Air Products Ltd, 99.9% purity) were used directly from the cylinders as supplied.

Catalysts

Catalyst samples were prepared from BDH Analar cupric oxide, with a stated purity of >98%. The major impurities were iron (0.05%) and sodium, potassium, and calcium (all <0.02%). The oxide (typically 1.72 g) was reduced by heating from ambient temperature to 508 K, at a rate of 1 K/min, in a flow of 6% (v/v) hydrogen in helium (flow rate = 25 ml/min). To complete the reduction the catalyst was subjected to a flow of 5.5% (v/v) carbon monoxide in helium (flow rate = 25 ml/min) for 200 s. Before the catalyst was used, any carbon monoxide adsorbed on the surface following the latter treatment was desorbed in a helium stream. Reactive frontal chromatography

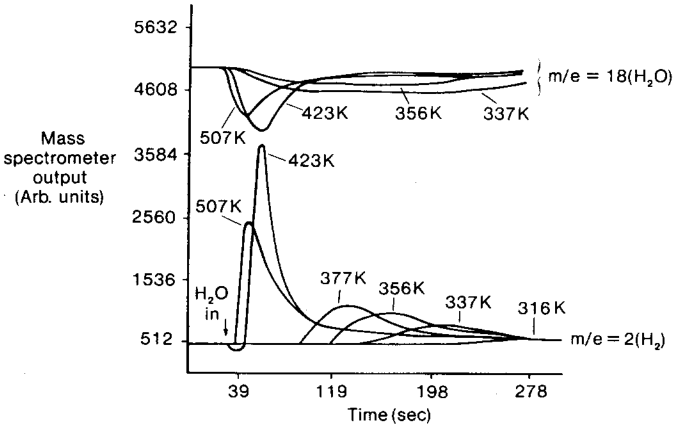

FIG. 2. Evolution of dihydrogen, and uptake of water, resulting from the reactive adsorption of water on polycrystalline copper in the range 316–507 K.

using nitrous oxide (*17*) gave an initial surface area of 2.34 m^2/g Cu. After use, the copper area had descreased to 1.27 m^2/g Cu.

The experimental apparatus used in these studies also allowed the BET surface area of the copper sample to be determined *in situ* (*8*). It was found that, at all stages of the experimental program, the copper surface area as measured by nitrogen adsorption at 77 K was identical, within experimental error, to that determined by nitrous oxide decomposition at 333 K. This is good evidence for little, if any, segregation of bulk impurities to the copper surface.

3. RESULTS

Reactive Adsorption of Water on Polycrystalline Copper

Detailed information regarding the decomposition of water on copper, over a wide temperature range, was obtained by a mass spectrometric analysis of dihydrogen evolution during the adsorption process. Figure 2 shows the variation of the $m/e = 2$ peak as a 25 ml/min 1.5% water–helium stream was switched from the bypass through the catalyst bed at various temperatures. At relatively high temperatures a sharp dihydrogen pulse was eluted from the catalyst after a period of 20–30 s. As the temperature of the catalyst was decreased, the time of evolution of the dihydrogen pulse increased and, correspondingly, the shape of this feature became more diffuse. At ambient temperature, no definite dihydrogen pulse was observed although, after 15 min on stream, some evidence for the formation of a small amount of dihydrogen was obtained.

Also shown in Fig. 2 is the uptake of water at the various temperatures. The shapes of these uptake curves showed a temperature dependence similar to that of the dihydrogen pulses. The activation energy for the reaction

$$H_2O(g) \rightarrow H_2(g) + O(ads)$$

may be calculated from the temperature dependence of the time of the initial evolution of dihydrogen, the net amount of water decomposed being negligible. A plot of $\ln(t[H_2] - t_0)$ against $1/T$, where $t[H_2]$ = time taken for the evolution of a known concentration of gas-phase dihydrogen; t_0 = dead (or sweepout) time of the system, and T = temperature (K), gives the activation energy for the production of these limited quantities of dihydrogen as 38 kJ/mol.

From the quantity of hydrogen produced at each temperature and a knowledge of the maximum oxygen surface coverage, as determined by nitrous oxide decomposition at 333 K, it was possible to calculate the frac-

TABLE 1

Reactive Chemisorption of Water on Polycrystalline Copper

Reaction number	Temperature (K)	Time in flow (min)	Time of hydrogen evolution[a] (s.)	Oxygen coverage from H_2 evolved[b]	Total oxygen coverage[c] (%)	Corrected oxygen coverage[d] (%)
1	297	22	—	—	51	20
2	316	10	340	—	33	19
3	325	10	230	—	28	14
4	357	10	125	4	28	14
5	377	10	90	5	28	14
6	423	15	32	8	36	15
7	507	15	21	7	>100	100

[a] Time taken for peak maximum to be obtained.

[b] Calculated as percentage of N_2O monolayer from yield of hydrogen desorbed.

[c] Calculated from subsequent CO titration, expressed as percentage of N_2O monolayer.

[d] CO titration values corrected for 0.016% oxygen impurity in feed gas, expressed as percentage of N_2O monolayer.

tional oxygen coverage assuming complete dissociation of the adsorbed water. Unfortunately, due to the "smearing" of the dihydrogen peak at the lower temperatures, quantitative estimations were not possible for the low coverages obtained at these temperatures. The results are summarized in Table 1.

Also shown in Table 1 are the total quantities of oxygen, quoted as fractional coverage relative to nitrous oxide decomposition, titrated from the surface by carbon monoxide reduction following each adsorption experiment. Since these values give the total oxygen surface coverage, from both the water decomposition and the adventitious 0.016% dioxygen impurity in the water–helium stream, a correction to allow for the latter was made. The corrected values are also shown in Table 1.

Temperature-Programmed Desorption following the Adsorption of Water on Polycrystalline Copper at 297 K

A 0.47% (v/v) water-in-helium stream was allowed to flow over a freshly reduced copper surface for 22 min at 297 K. At the end of this period it was noted that the amount of dihydrogen eluting from the catalyst column was in excess of that expected from the cracking of water in the mass spectrometer. The catalyst column was flushed briefly with helium before the temperature was ramped at 8 K/min to 483 K. The desorption profile, determined by mass spectrometric analysis of the reactor eluant, is shown in Fig. 3, from which it can be seen that a broad water desorption peak was obtained in the range 303–433 K. The quantity of water desorbed (1.39×10^{18} molecules, or a coverage of 3.5×10^{13} or 6.4×10^{13} molecules/cm^2 of the initial or final copper

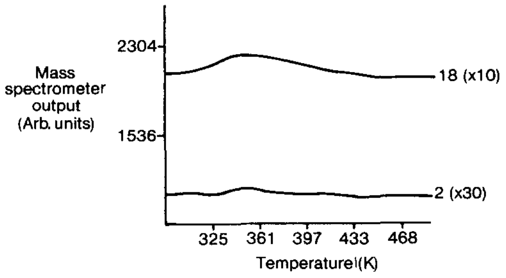

FIG. 3. Temperature-programmed desorption spectrum resulting from the adsorption of water on polycrystalline copper at 297 K.

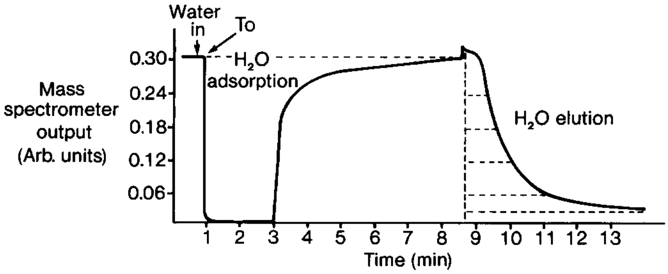

FIG. 4. Adsorption and subsequent desorption of water from a polycrystalline copper surface as monitored by gas adsorption chromatography (T_0 is sweepout time of system).

areas, respectively) corresponds to ~10% of the maximum uptake of water at 297 K. A dihydrogen desorption peak was also observed in the same temperature range.

Thermodynamics of the Adsorption of Water, Accompanying Its Decomposition, on Initially Clean Polycrystalline Copper

Gas adsorption chromatography was used to determine the adsorption isotherms generated by the interaction of water with a fully reduced copper surface. A typical adsorption/desorption profile is shown in Fig. 4.

Over the temperature range used in this study (316–377 K) it was found that, following gas–surface equilibration in a 0.36% water-in-helium stream, a large proportion of the adsorbed species only slowly desorbed from the copper surface in the helium flow, as shown by the elongated tails of the desorption profiles. Thus, although the adsorption isotherms were determined (Fig. 5), little detail in the low-coverage range could be obtained and, as a consequence, an accurate determination of the isosteric heat to these coverages was impossible.

Assuming the adsorption obeys the Langmuir equation, the number of adsorbed molecules which correspond to monolayer coverage (V_m) may be calculated from

$$p/V = (1/V_m) \cdot p + 1/(kV_m)$$

where p = concentration of adsorbate in the gas phase (mol/cm^3), V = volume adsorbed (cm^3), and $k = A \exp(\Delta H(\text{ads}/RT)$. The isotherms in Fig. 5, linearized according to above equation, are shown in Fig. 6. The gradients of these linearized isotherms are $1/V_m$ and from Fig. 6 it can be seen that these vary both with temperature and pressure.

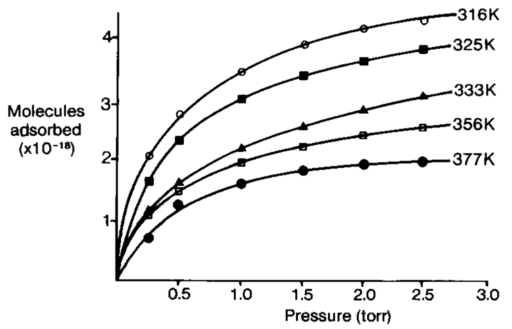

FIG. 5. Adsorption isotherms for the uptake of water on polycrystalline copper in the range 316–377 K.

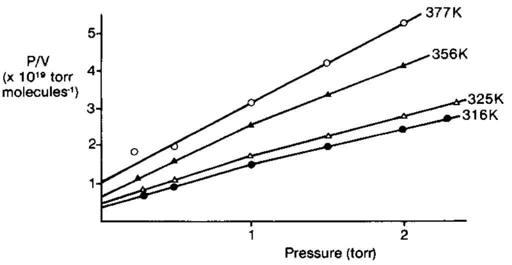

FIG. 6. Water adsorption isotherms linearized with respect to the Langmuir equation. The gradient of these plots is calculated to be the reciprocal of the number of adsorbed molecules corresponding to monolayer water coverage.

Below a partial pressure of 1 Torr, the numbers of molecules corresponding to monolayer coverage are 7.83 × 10^{18} (316 K), 7.24 × 10^{18} (325 K), 5.21 × 10^{18} (356 K), and 4.69 × 10^{18} (377 K), whereas above a partial pressure of 1 Torr, the corresponding values are 1.03 × 10^{19} (316 K), 9.38 × 10^{18} (325 K), 6.12 × 10^{18} (356 K), and 4.69 × 10^{18} (377 K). If the copper surface remained unchanged over this range of temperatures, the fact that the monolayer adsorbate volume is not constant could not be satisfactorily explained. However, the copper surface is likely to be oxidized to a different extent at each temperature and, since different bonding modes of water have been observed on reduced and oxidized copper surfaces (*13*), this is sufficient to explain the variation in the calculated values of V_m. An estimation of the average heat of adsorption across the whole surface can be made using the Langmuir equation $\Theta = kp/1 + kp$, where $k = A \exp(\Delta H(\text{ads})/RT)$. The fractional water coverages (Θ) are calculated from the ratio of the surface area covered by the water adsorbate [taken as the number of molecules adsorbed × the van der Waals (*18*) area (10.6 Å^2)] to the total copper surface area as determined by nitrous oxide decomposition. Taking the A factor ratio as unity when the partial pressures are expressed in mol/cm^3, a value of 45 kJ/mol is obtained for the average heat of adsorption of water.[1]

Temperature-Programmed Reaction of Carbon Monoxide and Water on Polycrystalline Copper

A helium stream containing, by volume, 4.6% carbon monoxide and 1.4% water was allowed to flow over a fully reduced copper surface for 15 min at 298 K. Analysis of the reactor eluant (Fig. 7) shows that as soon as the reaction mixture contacted the catalyst, a small quantity of carbon dioxide, corresponding to 4% of a monolayer of surface oxygen, was produced. However, no formation of dihydrogen was detectable.

Figure 7 also shows that during the adsorption of water and carbon monoxide onto the copper surface at 298 K (shown by decreases in the $m/e = 18$ and $m/e = 28$ peaks) prolonged exposure leads to water displacing carbon monoxide from the surface (indicated by an increase in the $m/e = 28$ peak). The amount of carbon monoxide displaced corresponded to 2.3 × 10^{18} molecules, equivalent to 13% of the maximum uptake of carbon monoxide.

Subsequent ramping of the catalyst temperature to 423 K at a rate of 8 K/min resulted in the immediate formation of dihydrogen as shown in Fig. 7. Some water desorption was observed while, concomitant with this desorption, 1.54 × 10^{18} molecules of carbon monoxide were readsorbed, thereby confirming the competitive adsorption of these gases on the copper surface.

At 353–363 K the rate of the forward shift reaction was significant. At very low conversions, where the concentrations of the reactant species can be considered to be invariant, analysis of the lineshapes of the product carbon dioxide and dihydrogen profiles gave an activation energy for their formation of 67–75 kJ/mol.

The catalyst column was allowed to cool from 423 K to ambient temperature in the carbon monoxide–water–helium stream, flushed with helium, and then heated at a rate of 8 K/min to 505 K. The resultant desorption profile is shown in Fig. 8, from which it can be seen that, in addition to a broad water desorption peak centered at 386 K, dihydrogen and carbon dioxide desorbed simultaneously with a coincident $T_{\max}$ of 413 K.

Reaction of Carbon Monoxide and Water on Copper at 335 K

When a helium stream containing 4.48% (v/v) carbon monoxide and 1.18% water was passed through a column of fully reduced

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[1] The adsorption A factor can be approximated by a standard collision number, $z = \pi\sigma^2 N(8kT/\mu)^{1/2}$, which has a value of ~$10^{13}$ in units of cm^{-3} mol^{-1} s, while the desorption A factor (kT/h) in units of s^{-1} has a value of ~10^{13}. The ratio is therefore unity.

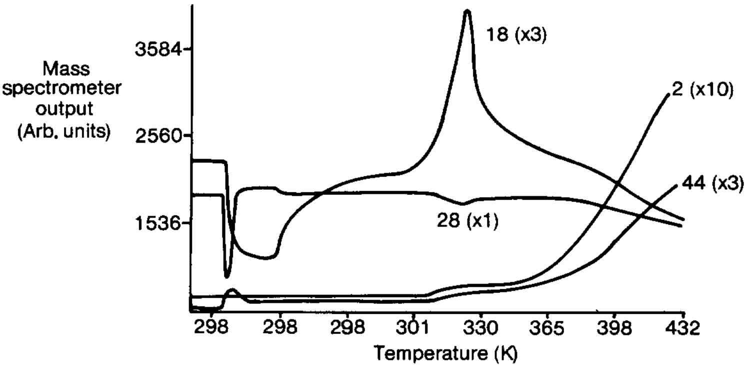


FIG. 7. Temperature-programmed reaction spectrum resulting from the interaction of a 4.6% CO–1.4% water–helium feedstream with polycrystalline copper. The reaction mixture was allowed to contact the copper catalyst for a period of 15 min at 298 K before ramping the temperature (at 8 K/min) to 423 K.

copper at 335 K, the reaction reached a steady-state conversion of 2.7% after 3 min, as shown in Fig. 9. Assuming that all the exposed copper atoms, as determined by nitrous oxide decomposition at 333 K, are active for this reaction, this corresponds to a steady-state turnover frequency (TOF) of 2.78×10^{-4} molecules site^{-1} s^{-1}. Before the catalyst steady-state condition had been reached a pulse of carbon dioxide was eluted from the column, followed 48 s later by a dihydrogen pulse.

Temperature-programmed desorption analysis of the copper surface after 30 min reaction under these conditions showed a broad water desorption peak ($T_{\text{max}} = 346$ K), a carbon dioxide desorption peak ($T_{\text{max}} = 400$ K), and diffuse dihydrogen desorption in the temperature range 320–381 K (Fig. 10).

4. DISCUSSION

The production of dihydrogen by the adsorption and reaction of water on reduced copper powder, as shown in Fig. 2, is convincing evidence for a dissociative chemisorption of water on the polycrystalline surface. A distinctive feature of this interaction, which is especially pronounced at elevated temperatures, is the fact that dihydrogen evolution occurs in two stages. Initially, rapid production of a limited quan-

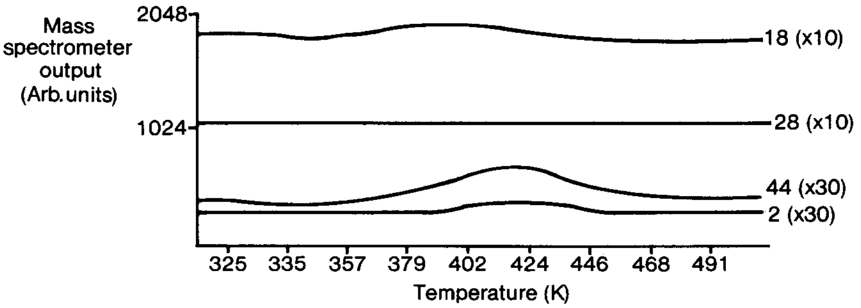


FIG. 8. Temperature-programmed desorption spectrum from a polycrystalline copper catalyst which had been producing CO_2 and H_2 from a CO–water feedstream at 423 K. The catalyst was cooled to ambient temperature under the reaction mixture prior to desorption analysis.

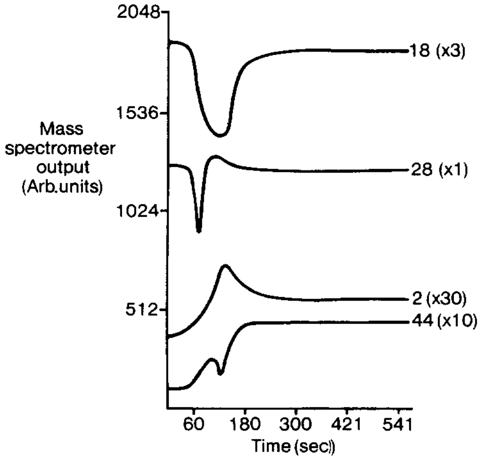


FIG. 9. Reaction of a CO–water–helium feedstream with polycrystalline copper at 335 K.

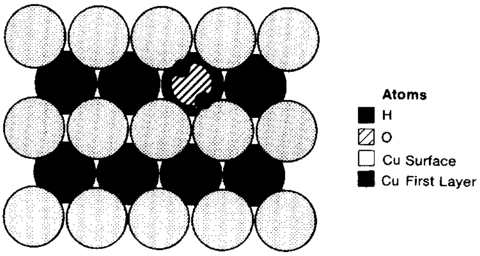


FIG. 11. Representation of the adsorption of a molecular water species in the fourfold hollow site on a Cu(110) surface (plan).

tity of dihydrogen is seen which, if we assume complete dissociation of the molecular water adsorbate between 423 and 507 K (Table 1), indicates a coverage of 7–8% of a monolayer of adsorbed oxygen. Thereafter, far slower production of dihydrogen and, consequently, adsorbed oxygen was evident. This rapid evolution of a small quantity of dihydrogen indicates, as previous studies had indicated (*2, 11, 12–14*), that the dissociative adsorption of water on copper is surface structure sensitive.

The structure sensitivity of the decomposition of water on copper can be readily understood by reference to the molecular models in Figs. 11–14. Figure 11 shows a water molecule bonded to a copper(110) surface. The water bonds via the lone pair of electrons on the oxygen *p*-orbital (*13*), most probably to a copper atom in a fourfold hollow site in the first layer. (The dimensions used in this representation are the covalent radii for oxygen and hydrogen and the atomic radius of copper.) Looked at in elevation (Fig. 12), it becomes clear why this surface will decompose water as there is easy interaction between the hydrogen atoms of the water and the topmost copper atoms.

The bonding of water to the next most open face of copper [the (100) face] is shown

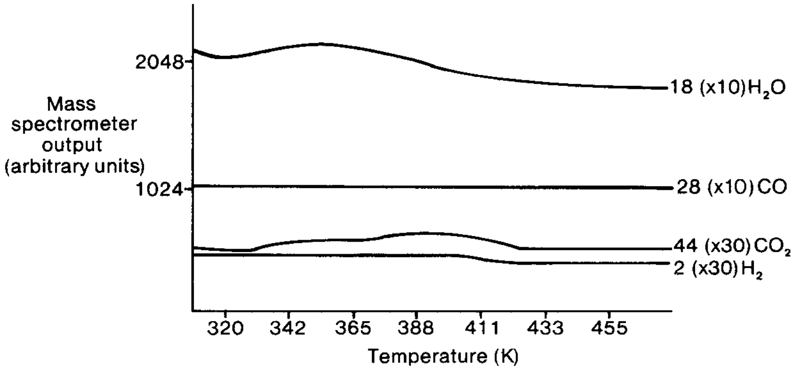


FIG. 10. Temperature-programmed desorption spectrum resulting from a polycrystalline copper surface which had been producing CO_2 and H_2 from a CO–water feedstream at 335 K. The catalyst was cooled to ambient temperature prior to desorption analysis.

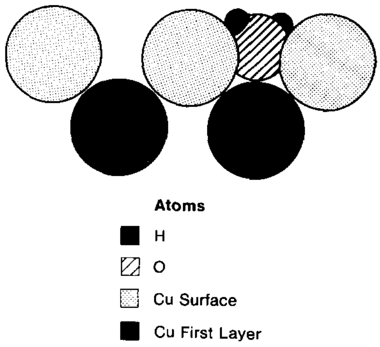


FIG. 12. Representation of the adsorption of a molecular water species in the fourfold hollow site on a Cu(110) surface (elevation).

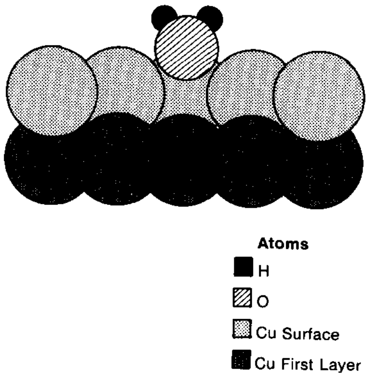


FIG. 14. Representation of the adsorption of a molecular water species in the fourfold hollow site on a Cu(100) surface (elevation).

in Fig. 13. As for the (110) surface the water is bonded to a first-layer copper atom in a fourfold hollow site by the oxygen lone-pair electrons. However, when viewed in elevation (Fig. 14), it is clear that there is little possibility of interaction of the hydrogen atoms of the water with the topmost copper atoms. On the close-packed (111) surface, the hydrogen atoms are even more removed from the surface copper atoms.

Further evidence for the heterogeneity of the polycrystalline surface with respect to water adsorption comes from an examination of the Langmuir plots in Fig. 6. These show good linearity in the medium to high pressure range and allow the average heat of water adsorption, at these surface coverages, to be calculated as 45 kJ/mol. This compares well with the values of 34 and 42 kJ/mol previously associated with the adsorption of molecular water species on Cu(111) surfaces (*2*, *12*). At low surface coverages, however, the p/V values are smaller than expected from a simple extrapolation of the high-coverage plots. This implies larger adsorbed volumes, V, and heats of adsorption, in this coverage region, than predicted for the majority of the copper surface. It is possible that this relatively small number of highly active sites may allow a facile dissociation of the molecular species, as evinced by the rapid dihydrogen evolution described previously.

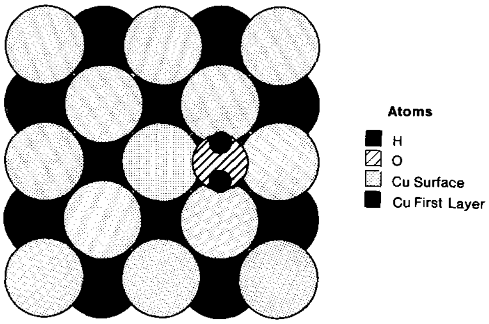


FIG. 13. Representation of the adsorption of a molecular water species in the fourfold hollow site on a Cu(110) surface (plan).

A further indication of the strength of the chemisorption process at low surface coverage can be obtained by consideration of the TPD profile shown in Fig. 3. This reveals that, following the adsorption of water on copper at 297 K, 10% of the total quantity of adsorbate did not desorb from the surface until temperatures of 303–433 K were attained. We have no direct evidence as to the nature of this strongly chemisorbed species. It is unlikely, however, that this is a molecular water species since no previous studies of the water–copper system have produced any evidence for the existence of a molecular water species with a heat of adsorption in the range 80–100 kJ/mol. It is more likely that the interaction of water with the adsorbed oxygen, produced by water decomposition and adventitiously acquired from the O_2 in the water stream, generates hydroxyl species on the copper surface (*12*). On heating, an activated disproportionation of the adsorbed hydroxyl groups will provide molecular water desorption as has been previously suggested (*13*). It is our belief that, despite the presence of a small percentage (0.016%) of oxygen in the water stream, a direct interaction of adsorbed water with suitable copper surface sites can facilitate water decomposition. It is known that adsorbed oxygen can enhance the propensity of a copper surface for water decomposition (*11*). However, the fact that we have found that only a small number of sites allow a transient facile decomposition of water indicates that the oxygen contaminant in the water stream is not responsible for the generation of these decomposition sites. If the oxygen was responsible for this facile decomposition path, the evolution of hydrogen would not be transient in nature since oxygen was fed continuously into the reactor with the water adsorbate. Furthermore, oxygen appears to promote the decomposition by altering the adsorption geometry of the water molecule and does not become directly involved in the hydroxylation reaction (*13*). This appears to confirm the fact that the bonding geometry of the water molecule controls its reactivity.

A reaction scheme consistent with the above observations and the published literature follows:

$$H_2O(g) + Cu \rightarrow H_2O(ads) \quad (1)$$

$$H_2O(ads) + Cu \rightarrow OH(ads) + H(ads) \quad (2)$$

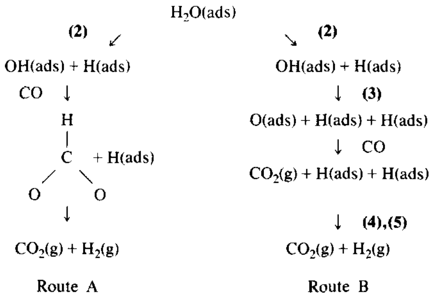
$$OH(ads) + Cu \rightarrow O(ads) + H(ads) \quad (3)$$

$$H(ads) + H(ads) \rightarrow H_2(ads) + 2Cu \quad (4)$$

$$H_2(ads) \rightarrow H_2(g) + Cu \quad (5)$$

$$H_2O(ads) + O(ads) \leftrightarrow OH(ads) + OH(ads) \quad (6)$$

The temperature dependence of the rate of production of the initial dihydrogen pulse, on contact of water with polycrystalline copper, indicates that an activation energy of 38 kJ/mol is associated with reactions (1)–(5). It is therefore not surprising that the reaction of water with copper at ambient temperature produces gas-phase dihydrogen only after a considerable time delay. However, the TPD profile shown in Fig. 3 reveals that, despite a slow production of gas-phase dihydrogen, a significant concentration of adsorbed atomic hydrogen exists on the copper surface. This fact forces us to consider the possibility that the activation energy associated with the production of gas-phase dihydrogen is not due to water decomposition [reactions (1)–(3)] but, at room temperature, may be associated with the recombinative desorption of hydrogen from the copper surface [reactions (4) and (5)]. Further evidence as to the rate-determining step in the total mechanism is obtained from consideration of the effects of the addition of carbon monoxide to the water–copper system. Figure 7 shows that when a feed gas containing both water and carbon monoxide was passed over polycrystalline copper at ambient temperature dihydrogen gas was not produced. However, carbon dioxide was instantly eluted from the catalyst column. This corresponded to the removal of ~4% of a monolayer of surface oxygen. Before the experiment was started, the copper surface was fully reduced by reaction with carbon monoxide at 473 K, the temperature being lowered to ambient under a flow of helium. The surface can, therefore, be considered free of oxygen before the water–carbon monoxide stream entered the catalyst column. The feedstream was known to contain 0.016% oxygen impurity, which would readily allow carbon dioxide formation. However, the quoted value of 4% of a monolayer of oxygen removed by carbon monoxide has been calculated taking into account this fractional impurity. The sticking probability of the dissociative chemisorption of oxygen is considered to be unity in these calculations. Almost all the



SCHEME 1. Boldface numbers in parentheses are reaction steps previously given.

available literature evidence shows that the oxygen is unlikely to arise from dissociative chemisorption of carbon monoxide (*19, 20*); hence it is apparent that the excess carbon dioxide must have been derived from the interaction of carbon monoxide with a water-generated oxygen species. There are two possible routes by which water and carbon monoxide may interact to form carbon dioxide (see Scheme 1).

Route A describes a plausible mechanistic pathway involving the formation and subsequent decomposition of adsorbed formate. This intermediate has been considered as a likely product of the interaction of carbon monoxide and hydroxyl species on copper surfaces (*1*), although other studies have found no evidence for this reaction (*21*). At ambient temperature we believe that route A can play no part in carbon dioxide formation. We later discuss evidence which shows that carbon monoxide and water do not produce formate species on unsupported copper surfaces but, even if formate production is considered feasible, the kinetics of the formate decomposition process are such that the half-life of this species on a copper surface at ambient temperature is of the order of 10^{10}s (*22*). It is evident that the rate of production of carbon dioxide would be extremely slow at ambient temperature.

Route B therefore best describes the means by which carbon dioxide is generated by the interaction of carbon monoxide and water at ambient temperature, i.e., by a reduction of surface oxygen species generated by complete water decomposition. The kinetics of this surface reduction are known to be extremely favorable (*23*).

All this evidence suggests that, at ambient temperature, water decomposition is a facile process on a small fraction of the polycrystalline copper. It is apparent that the rate of production of gaseous dihydrogen is restrained by the recombinative desorption of atomic hydrogen from the copper surface. Hence, the activation energy (38 kJ/mol) associated with the production of this limited quantity of dihydrogen can be attributed to the recombinative desorption of atomic hydrogen [reaction steps (4) and (5)]. Furthermore, since only a finite quantity of carbon dioxide was produced by the reaction of carbon monoxide and water at ambient temperature, it is likely that adsorbed hydrogen can poison those sites which readily allow dissociative water chemisorption. The continuous slight, but not inconsiderable, production of dihydrogen, which follows the elution of the dihydrogen transients shown in Fig. 5, suggests a further slow decomposition of water on the copper surface. However, the quantities of oxygen titrated from the surface on completion of each reaction do not correlate with the total integrals of dihydrogen evolution (Table 1). A marked discrepancy is obvious at low temperatures, while at 507 K a surprising inconsistency is apparent. Under these conditions, a route must exist which permits the dissociative adsorption of water without the concomitant desorption of dihydrogen.

There are two means by which hydrogen retention may occur. First, the reaction of atomic hydrogen with adsorbed oxygen will produce hydroxyl species which are likely to have a significant lifetime on the copper surface. This will delay, or prevent, hydrogen desorption processes. Second, recent evidence from LEED and atomic diffraction studies (*24*) has demonstrated the possibility that adsorbed hydrogen will, rather than desorb, migrate to the subsurface and cause reconstruction of the copper surface. This reaction, which is temperature dependent, may account for the slightly lower quantities of dihydrogen evolved on contact of water with polycrystalline copper at 507 K (Table 1). A similar hydrogen trapping mechanism is postulated to occur in a copper–zinc oxide–alumina catalyst under methanol synthesis conditions (25).

The data presented in Table 1 show no obvious correlation between reaction temperature and the quantity of adsorbed oxygen produced by water decomposition. It appears that, at moderate temperatures, a limiting degree of surface oxygen coverage persists. This may be caused by substantial blocking of surface sites by hydroxyl species. At 507 K, where greater than monolayer oxygen coverage was produced, lower surface concentrations of hydroxyl and molecular water species and diffusion of oxygen into the copper subsurface may allow a more facile accumulation of oxygen.

Relevance to the Water Gas-Shift Reaction

It is clear from this study and others (*2*, *11–13*) that the adsorption of water on copper shows distinct surface sensitivity. At room temperature it is apparent that a small fraction of the copper surface allows an extremely facile decomposition of water. In the presence of carbon monoxide, carbon dioxide is instantaneously produced and it is our contention that this reaction proceedes by reduction of atomic oxygen chemisorbed on the copper substrate (route B). Moreover, the atomic hydrogen generated by the dissociative chemisorption of water acts to poison further water decomposition. Therefore, at these low temperatures, the forward shift reaction is restrained by the unfavorable kinetics associated with the recombinative desorption of hydrogen.

This mechanism is also consistent with the data presented in Fig. 9. On contact of a carbon monoxide–water stream with polycrystalline copper at 335 K both carbon dioxide and dihydrogen were evolved. However, a comparison of the $m/e = 44$ and $m/e = 2$ plots in Fig. 9 shows that, in the early stages of the reaction, the rate of carbon dioxide production was greater than that of hydrogen evolution. A combination of rapid water decomposition and subsequent reduction of the surface with carbon monoxide, together with a rate-limiting regeneration of active copper sites (by slow hydrogen desorption), readily explains these experimental observations.

An associative interaction between carbon monoxide and water is unlikely, and completely unnecessary, to describe the mechanics of the above processes. However, these data, which were obtained at relatively low temperatures, do not preclude the operation of an associative mechanism at more typical reaction temperatures of 500 K. Indeed, the characteristic coincident desorption profiles of carbon dioxide and dihydrogen shown in Fig. 8, which were obtained after the shift reaction had been run at elevated temperatures, indicate a substantial coverage of formate species on the copper catalyst (*22*). However, previous studies have determined that carbon dioxide and dihydrogen will readily produce formate when coadsorbed on polycrystalline copper (*25*). In view of the relatively high water gas shift conversions reached in this experiment, it is possible that the formate arises from the interaction of carbon dioxide and dihydrogen, which are formed as products of the shift reaction.

In contrast, when the reaction is run at 335 K (Fig. 9) the conversion is far lower and product concentrations and/or readsorptions are not expected to be significant. However, the calculated rate of the shift reaction at this temperature (2.78×10^{-4} molecules $\text{site}^{-1}\ \text{s}^{-1}$) indicates that, after 30 min on stream, 85% of the surface sites will have completed one mechanistic turnover. The TPD profile produced after this reaction interval (Fig. 10) is that expected from a combination of the separate interactions of water with reduced copper (Fig. 3) and carbon dioxide with an oxidized copper surface (*26*). There are no formate species extant on the copper surface, as may have been expected if this is a genuine reaction intermediate, and these species cannot therefore be intimately involved in the progress of the forward shift reaction. These data show that carbon monoxide and water do not readily generate formate-type adsorbates on unsupported and unpromoted copper catalysts.

The mechanism by which carbon monoxide and water produce carbon dioxide and dihydrogen at 297 and 335 K is therefore a plausible means by which the reaction may proceed at elevated temperatures. No direct association of carbon monoxide and water is necessary in this synthetic pathway. Rather, sequential oxidation (by water) and reduction (by carbon monoxide) of a small fraction of the copper surface provide facile carbon dioxide evolution. At low temperatures (335 K) the rate of the reaction is limited by the recombinative desorption of atomic hydrogen from the highly active catalytic centers. At higher temperatures, the kinetics of the hydrogen desorption reaction (*27*) are such that the rate of the hydrogen recombination reaction is faster than the observed rate of the shift reaction. The rate-limiting step in the reaction will therefore change in the range 350–400 K to the water decomposition reaction. The activation energy of the forward shift reaction on polycrystalline copper (67–75 kJ mol^{-1}), which was determined by temperature-programmed reaction at 350–400 K, is in excellent agreement with literature values, obtained on several different copper surfaces, which have been tabulated by Campbell and Daube (*28*). This suggests that the mechanism of the reaction is the same on all of the differently prepared surfaces, despite the fact that the TOF of the reaction can show wide variation from surface to surface. For example, Campbell and Daube (*28*) have found the activity of a cesium-promoted Cu(111) surface to be at least 15 times greater than that of clean Cu(111), and an extrapolated value of the TOF we obtained on polycrystalline copper (2.74×10^{-4} molecule s^{-1} site^{-1} at 335 K) is two orders of magnitude greater than that on Cu(111). Furthermore, the activity, on a metal area basis, of a commercial LT shift catalyst is several orders of magnitude greater than those of the single-crystal and polycrystalline copper catalysts (*29*). None of the dramatic differences in activity observed on these copper catalysts can be attributed to changes in the activation energy of the reaction. Rather, it appears that the rate of the shift reaction is strongly dependent on the number and type of active sites on the catalyst surface. A surface, such as the (111), which has little propensity to dissociate water will show low activity for the shift reaction. However, the TOF on the (111) surface can be increased by cesium doping. This may be understood in terms of the creation of surface sites which allow more extensive water decomposition. The high TOF obtained on our polycrystalline sample and on the commercial catalyst could be explained by an increase in the preexponential factor in the rate equation due to the presence of a significant number of copper sites which facilitate a rapid dissociative chemisorption of molecular water. These sites, which constitute 7–8% of the available copper surface area on the unsupported polycrystalline copper, are likely to be those which allow an intimate interaction between adsorbed molecular water species and the copper adsorbent. The water gas shift reaction is clearly structure sensitive on copper catalysts, with the most favorable structural features being associated with "open" surfaces such as the (110).

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