

INTERACTION OF HYDROGEN WITH OXYGEN ON Cu(111)

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Received 24 February 1983; accepted for publication 26 August 1983

The kinetics of the interaction of hydrogen with oxygen adsorbed on Cu(111) up to 0.5 monolayer is studied with ellipsometry. It is shown that hydrogen dissociates at Cu sites and that an important step is the formation of $\text{OH}_{(\text{ad})}$ from $\text{O}_{(\text{ad})}$ and $\text{H}_{(\text{ad})}$ with an activation energy of 93 ± 12 kJ/mol. The operation of an ionization gauge changes the reaction mechanism in the sense that it facilitates hydrogen dissociation. In this case the overall activation energy is only 5 kJ/mol.

1. Introduction

The adsorption of oxygen on Cu single crystals [1–8] and the dissociative hydrogen chemisorption [9–11] have been studied extensively. Few investigations, however, are concerned with the reaction between hydrogen and oxygen on copper single crystal surfaces [12].

The interaction of carbon monoxide with oxygen adsorbed on copper surfaces has been studied [1–4] and from a catalytic point of view it is interesting to investigate whether there is a pronounced difference in the reactivity of preadsorbed oxygen towards carbon monoxide and hydrogen.

The present paper is concerned with the reaction between hydrogen and adsorbed oxygen (up to 0.5 monolayer) on a Cu(111) surface.

2. Experimental

The experiments were performed in a standard UHV system equipped with facilities for AES, LEED and ellipsometry. The surface was cleaned by cycles of sputtering (typically 500 eV Ar^+ , $5 \mu\text{A}/\text{cm}^2$, angle of incidence 45° , 35 min) and annealing (15 min, 450°C). Auger spectra showed less than 3% of a monolayer oxygen contamination on the Cu(111) surface. Ellipsometric measurements were carried out with an automatic nulling ellipsometer which continuously measured minima in polarizer and analyser settings as a function of time in one zone. Off null irradiance measurements were carried out for comparison with previous results [1].

The clean Cu(111) surface was covered with half a monolayer of oxygen, by exposing the surface to 780 L O₂ at a crystal temperature of 195°C. The saturation value of $\delta\Delta$ was $0.7 \pm 0.07^\circ$ which is in very close agreement with the results of Habraken et al. [1]. According to these results it can be concluded that the relation between the ellipsometric parameter $\delta\Delta$ and the oxygen coverage θ_o can be represented by the equation:

$$\theta_o = 0.7 \delta\Delta. \quad (1)$$

The kinetics of the oxygen adsorption confirm the dissociative adsorption via a mobile precursor state, as reported in ref. [1].

3. Results

The oxygen covered Cu(111) surface was exposed to hydrogen in the pressure range of 2×10^{-5} to 5×10^{-4} Torr, at crystal temperatures between 240 and 430°C, and at oxygen coverages between 0.2 and 0.5 monolayer. The reaction rate, starting with half a monolayer of oxygen was immeasurably small below crystal temperatures of 240°C and hydrogen pressures as high as 5×10^{-4} Torr. At higher crystal temperatures the reaction rate is independent of the temperature at which the clean Cu(111) surface was covered with oxygen. The preadsorbed oxygen was quantitatively removed from the copper surface after reaction with hydrogen.

Fig. 1 shows the change in the ellipsometric parameter $\delta\Delta$ starting with half a monolayer of oxygen on the Cu(111) surface at crystal temperatures ranging

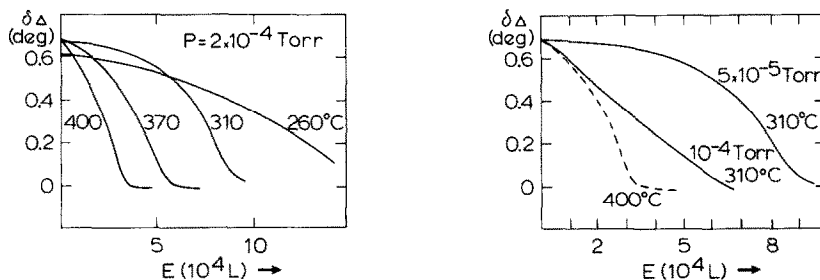


Fig. 1. Change in $\delta\Delta$ ($=1.4\theta_o$) upon removal of half a monolayer of oxygen from Cu(111) by hydrogen at 2×10^{-4} Torr. Crystal temperatures (in °C) are indicated in the figure. At 430°C the reaction curve is virtually identical to that of 400°C.

Fig. 2. Removal of half a monolayer of oxygen from Cu(111) by H₂. At lower crystal temperatures the reaction does not scale as $p \times t$ (solid lines). At higher temperatures the extent of the reaction is strictly proportional to the exposure.

from 260–430°C and at a hydrogen pressure of 2×10^{-4} Torr. When the reaction was started at a lower oxygen coverage, the corresponding part of the curve was reproduced. Between 370 and 430°C the extent of the reaction was proportional to $p \times t$. At temperatures below 370°C the $\delta\Delta$ versus exposure curves were no longer identical for different pressures of hydrogen. In fig. 2 the reaction curves are depicted at two crystal temperatures, 310°C and 430°C, for hydrogen pressures of 1×10^{-4} and 5×10^{-5} Torr.

The reaction rates were calculated as $d(\delta\Delta)/d(pt)$ from the linear parts of the reaction curves. It can be concluded that the reaction rate is first order with respect to the hydrogen pressure above 370°C.

The Arrhenius plot of the reaction probability, defined as the number of oxygen atoms removed per incident H_2 molecule, is given in fig. 3. It shows that the apparent activation energy, E_{act} , increases with increasing temperature. Phenomenologically two regions could be distinguished from the Arrhenius plot: $340 < T < 430^\circ\text{C}$ with $E_{act} = 65 \pm 5$ kJ/mol and $260 < T < 340^\circ\text{C}$ with $E_{act} = 5 \pm 2$ kJ/mol.

During the experiments we found that the ion gauge affected the reaction rate. All the results given above have been obtained with the ion gauge respectively switched on and off. The reaction curves with the ion gauge on were always straight lines in the whole temperature range of 260–430°C and the reaction rates were first order in the hydrogen pressure. Fig. 4 shows the effect of the ion gauge on the reaction at 400°C and hydrogen pressure 2×10^{-4} Torr. It is seen that the reaction probability is increased markedly, although its temperature dependence is rather small (see fig. 3, dotted line).

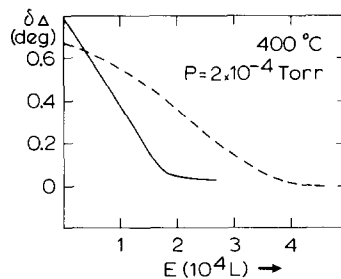
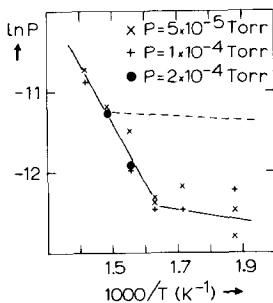
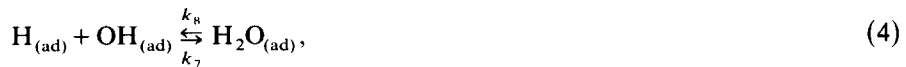


Fig. 3. Arrhenius plot of the reaction probability (P) as a function of $1/T$; P is defined as the number of oxygen atoms removed per incident hydrogen molecule. Dashed line: with ionization gauge operating. Solid line: ionization gauge switched off during reaction. Note that at low temperatures the reaction is pressure dependent if the ion gauge is switched off.

Fig. 4. Effect of an operating ion gauge on the reaction curve at 400°C, $p(H_2) = 2 \times 10^{-4}$ Torr: (—) gauge on; (---) gauge off.

4. Discussion

It is obvious from fig. 4 that the effect of an operating pressure gauge is significant in accelerating the reaction. Since the reduction involves atomic hydrogen, the effect of the ion gauge must be to facilitate the dissociation of H_2 . Similar effects have been reported for the adsorption of O_2 on Ag [13], the reduction of O/Ni(100) by H_2 [14], the decomposition of CO on Ni(100) [15] and the oxidation of C on Ni(100) by O_2 [16]. In all cases the breaking of an interatomic bond is easier for diatomics that have "seen" an operating ion gauge. This is not entirely a consequence of a decrease in the bond strength upon ion formation as can be seen from table 1. In contrast to CO and H_2 , the O_2^+ dissociation energy is actually larger than that for O_2 . It might, however, be linked to an increased stability of the molecular-ion precursor state due to its image force, analogous to the promotor function of K for the dissociation of N_2 on iron [18]. The higher rate of adsorption of atoms, particularly H atoms has of course been known for a long time [19,20], but since in our experimental set-up the pressure gauge is not in line of sight with the copper crystal, we believe that some excited or ionized molecular hydrogen species is involved in the reaction. In any case the general reaction scheme may be written as:



When the ionization gauge is operating the experimental results give a reaction curve which is first order with respect to the hydrogen pressure and zero order in the oxygen coverage (cf. fig. 4, solid line). This implies that adsorbed hydrogen atoms cannot be in equilibrium with adsorbed hydrogen molecules, since then a square root dependence on $p(H_2)$ would result. Also, a

Table 1

Dissociation energies D (in eV) of diatomics and their positive ion; from ref. [17]

CO	CO ⁺	O ₂	O ₂ ⁺	H ₂	H ₂ ⁺
11.1	9.9	5.1	6.5	4.5	2.6

zero order oxygen coverage dependence suggests a rate-limiting step before any reaction with adsorbed oxygen. A logical consequence is then to take $k_3[\text{H}_{2(\text{ad})}] \gg k_4[\text{H}_{(\text{ad})}]^2$ from which it follows that:

$$d[\text{O}_{(\text{ad})}]/dt = -\frac{2k_1k_3}{k_2 + k_3}p(\text{H}_2). \quad (6)$$

Eq. (6) describes the experiments with the pressure gauge on quantitatively. The reaction is zero order in $\text{O}_{(\text{ad})}$ and first order in hydrogen pressure. Its activation energy, 5 kJ/mol, is less than the activation energy of dissociative hydrogen chemisorption on copper, 12 kJ/mol [9] due to the pressure gauge effect. In fact, the present analysis is entirely analogous to that given for the reaction of oxygen with hydrogen on a Cu–Ni(110) alloy [21], the only difference being that in the latter case Ni sites, rather than the operating ion gauge, facilitate hydrogen dissociation.

The experiments with the ion gauge switched off are more difficult to interpret. The shape of the reaction curves (figs. 1 and 2) is clearly not described by eq. (6). Also a more general solution of eqs. (2)–(5), as given earlier [21], without the assumption that $k_3[\text{H}_{2(\text{ad})}] \gg k_4[\text{H}_{(\text{ad})}]^2$, always yields reaction curves that are either straight lines or exponential-like, but an increase in the reaction rate can never be reproduced. We are thus forced to make additional assumptions about the detailed mechanism. A clue as to where these additions may have to be made can in fact be obtained from the experimental data. The initial slow rate at high oxygen coverage suggests that the presence of oxygen does not enhance the dissociation of hydrogen, since in that case one would expect an initially large reaction rate, which decreases with decreasing oxygen coverage. Rather the reverse seems to be the case, oxygen blocking sites for hydrogen dissociation. Since in the temperature range 370–430°C the extent of the reaction is proportional to the exposure ($p(\text{H}_2) \times t$) no equilibrium between adsorbed hydrogen atoms and molecules exists. Qualitatively our results (figs. 1 and 2) are the same as those of Hachicha et al. [12] for Cu(110), who also report a proportionality with hydrogen exposure and a similar shape of the reaction curve. Thus the formation of OH groups on Cu/O must be much faster than the recombination of hydrogen atoms on the surface. The results of Pritchard [22], who found reversible adsorption of H_2 on Cu around room temperature, are not at variance with this conclusion. The hydrogen atom concentration in our case of high temperature will be extremely small and encounters between two H atoms will be much more infrequent than between an adsorbed H and O atom.

The simplest way of taking all this into account is to put:

$$k_3 = k'_3(1 - \theta_{\text{O}}), \quad k_4 = 0, \quad (7)$$

which implies that hydrogen dissociation only occurs on pure copper sites. Using the stationary state condition for adsorbed hydrogen molecules a

numerical solution of eqs. (2), (3) and (7) is possible. In the temperature range 370–430°C, where the apparent activation energy is about 65 kJ/mol, good fits to the observed reaction curves could be obtained by this procedure. This is

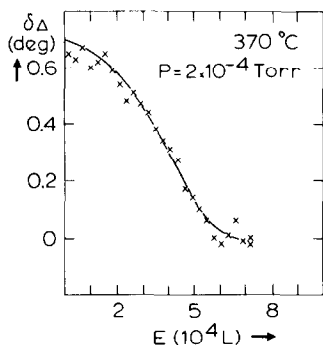


Fig. 5. Comparison of observed (×) and calculated (—) reaction curve for oxygen removal from Cu(111); $p(\text{H}_2) = 2 \times 10^{-4}$ Torr, $T = 370^\circ\text{C}$.

illustrated in fig. 5. As usual in kinetic studies, this success only makes our mechanism, viz. dissociation of hydrogen on pure copper sites and no hydrogen dissociation equilibrium, a probable and not impossible one. It does, however, account satisfactorily for the observed data.

From the calculations the activation energy of k_5 , the formation of OH groups from $\text{O}_{(\text{ad})}$ and $\text{H}_{(\text{ad})}$, could be extracted. Its value is 93 ± 12 kJ/mol. This is about equal to the value reported by Hachicha et al. [12], viz. 82 ± 6 kJ/mol, for the same reaction on Cu(110). On Cu–Ni(110) the activation energy for this process has also been given as 80 kJ/mol, if the reaction takes

Table 2

Reaction probabilities for the oxidation of CO and H_2 on copper surfaces and their activation energies; data taken from refs. [1–4,12] and the present work

	$p(\text{CO})$	$E_{\text{act}}(\text{CO})$ (kJ/mol)	$p(\text{H}_2)$	$E_{\text{act}}(\text{H}_2)$ (kJ/mol)
Cu(111)				
350°C	1.4×10^{-4}		5.2×10^{-6}	
440°C	3.1×10^{-4}	33	2.4×10^{-5}	65
Cu(110)				
350°C	7.9×10^{-5}		3×10^{-7}	
440°C	9.8×10^{-5}	26	2×10^{-6}	82
Cu(100)				
350°C	2.2×10^{-5}		4.5×10^{-5}	
440°C	4.5×10^{-5}	29	–	–

place on copper sites [21]. We can thus conclude that the hydrogen–oxygen reaction on Cu surfaces is determined by the initial formation of adsorbed OH groups (with activation energies in the range 80–92 kJ/mol) and that the reaction is not particularly plane-specific. Similar conclusions have been drawn with respect to the CO oxidation on the low index copper faces [4]. The activation energy for the Langmuir–Hinshelwood reaction of adsorbed CO and O is 75–84 kJ/mol, independent of the crystallographic orientation. The reaction probabilities, however, are different for H₂ and CO. Table 2 summarizes these probabilities at 350 and 440°C and their corresponding activation energies. It is seen that, at least for the two surfaces where data are available, carbon monoxide is oxidized much more readily than hydrogen. Also the more densely packed (111) face is more easily reduced than the less dense surfaces by both reactants.

Acknowledgements

The authors thank Mr. A.J.M. Mens for technical assistance. The investigations were supported by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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