Dissociative hydrogen adsorption and its reaction with oxygen on Cu(110)

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Abstract. Supersonic molecular beam techniques have been used to investigate the reaction between hydrogen and a (2×1) oxygen overlayer on Cu(110). The reaction has been studied as a function of surface temperature T_s and incident beam translational energy. The rate of water production is undetectably low for a room temperature H_2 beam ($E_\perp = 69$ meV), and remains so until the normal component of the beam energy is increased to $E_\perp \sim 200$ meV. For $E_\perp > 200$ meV one observes H_2O production with kinetics which reflect a Langmuir–Hinshelwood reaction mechanism, and the surface reaction continues to completion. The results suggest that the dissociative barrier accessed with translational energy can be rate determining, and the barrier itself is insensitive to oxygen coverage. Once this barrier is overcome, the surface reaction exhibits a T_s dependence and an activation energy which varies with oxygen coverage in the range 0–60 kJ mol^{-1}.

1. Introduction

The oxygen (2×1) overlayer on Cu(110) can be removed entirely by its reaction with H_2 or CO. Both the H_2 and CO reactions are characterised by a Langmuir–Hinshelwood reaction mechanism [1–3], and exhibit surface temperature (T_s) dependent rates which yield very similar 'activation energies' [1, 2]. Despite these observations, the reaction probabilities at comparable values of T_s are two or three orders of magnitude different [2], with the probability of the hydrogen reduction considerably lower, and in the range 10^{-7} at 500 K to 10^{-5} at 800 K. Despite this discrepancy it was concluded that the rate-dermining step in both cases above involved a surface reaction step, and it was assumed that the dissociative adsorption of hydrogen was fast and not rate limiting. The latter assumption was based primarily on the evidence of molecular beam studies [4] which place a one-dimensional potential barrier for dissociative hydrogen adsorption at $\sim$120 meV on Cu(110).

We have used a supersonic molecular beam source of hydrogen to study its reaction with the oxygen (2×1) overlayer on Cu(110) to produce water. This technique enables us to separate the role of any activation barrier associated with dissociative hydrogen adsorption from barriers associated with subsequent surface reaction processes. An implicit assumption is that the activation barrier to dissociation is accessible with translation energy [4].

2. Experimental procedure

The experiments were carried out in an ultrahigh-vacuum system designed for both elastic and reactive scattering of atom–molecular beams at surfaces. A brief description
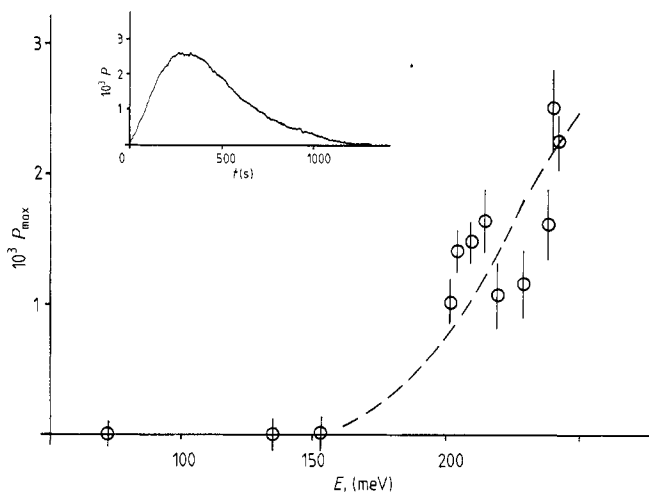
Figure 1. The maximum reaction probability P_{max} as a function of normal beam energy $E_\perp$. The surface temperature $T_s \approx 650$ K. The inset shows the reaction itself as a function of time for $T_s = 667$ K and $E_\perp = 214$ meV.

of the system can be found elsewhere [5]. The supersonic beam was produced by expansion of H_2 in an 80 μm diameter nozzle in front of a 0.31 mm diameter skimmer orifice. The final aperture was chosen to produce a beam diameter at the sample of 10 mm, and the beam flux was $\sim 6 \times 10^{14}$ molecules cm^{-2} s^{-1}. Two quadrupole mass spectrometers were available in the UHV chamber, one of which was fixed and the other differentially pumped and free to move in two azimuthal planes.

The Cu(110) crystal was cleaned initially by cycles of Ar$^+$ ion bombardment at $T_s = 700$ K followed by annealing at 850 K. Subsequent cleaning to remove adsorbed oxygen was achieved by a surface reduction using deuterium atoms produced from D_2 by a hot filament and doser source 20 mm from the sample, which was kept at $T_s = 700$ K. Sample cleanliness and order was confirmed using He atom scattering [6], with the same scattering criteria as used in previous studies [5, 6].

3. Results and discussion

Oxygen was adsorbed on the Cu(110) surface to produce the well known [7] (2 × 1) overlayer which was characterised by LEED. The adsorption was carried out at $T_s = 400$ K and typically an exposure of 10^{-5} Torr s was used to ensure a well ordered overlayer at $\theta_{oxygen} = 0.5$. Once the overlayer was adsorbed, the hydrogen beam was flagged open to impinge on the surface. Initial experiments were carried out with the beam impinging along the surface normal.

At low translation beam energies ($E_\perp < 200$ meV) there was no detectable reaction to produce H_2O at $T_s = 700$ K. As the energy was increased, the rate of reaction sharply increased at $E_\perp \approx 200$ meV, and reactions carried out above this energy would lead to a complete reduction of Cu(110)–O(2 × 1) to produce the clean Cu(110) surface. The kinetics for the reaction, once observed at $E_\perp \gg 200$ meV for $T_s = 667$ K is shown in the inset in figure 1. The shape of the non-steady state curve is characteristic of a Langmuir–Hinshelwood mechanism, with the rate limited by the concentration of active sites for dissociative hydrogen adsorption at high θ_{oxygen}, and limited by the oxygen concentration

itself at low θ_{oxygen}. The shape is similar to that observed for the CO reduction of the same oxygen overlayer [8]. Since the area under the curve (inset, figure 1) is proportional to the number of desorbed water molecules, which is given by the oxygen coverage (assuming reaction goes to completion), and the beam flux is known, the experiment allows the calculation of absolute reaction probabilities. Figure 1 shows a plot of the maximum reaction probability observed as a function of incident beam energy $E_\perp$ at $T_s = \sim 700$ K. It appears that the reaction is rate limited by the dissociation of H_2 at low beam energies. This would be the first step in the reaction mechanism in the Langmuir–Hinshelwood scheme:

$$H_{2(g)} + O_{(a)} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2H_{(a)} + O_{(a)}.$$
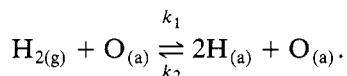
The relatively sharp rise in reaction rate at $E_\perp = 200$ meV implies an activation barrier for hydrogen dissociation $E \geqslant 200$ meV which can be accessed with translational energy. We have performed experiments at incident angles away from normal and shown that it is indeed the *normal component* $(E_\perp)$ of translational energy which is important in accessing this barrier under reaction conditions. The normal energy scaling is similar to results obtained on the clean Cu(110) surface [4], although the barrier in the latter case was observed at the significantly lower energy of $E \approx 120$ meV.

Comparison of an apparent dissociative barrier for H_2 adsorption in the entrance channel in the clean [4] and oxygen-covered surface may be quite different. Furthermore, a barrier which was a function of θ_{oxygen} could significantly influence the observed kinetics in a non-steady state experiment. An increase in the barrier height during reaction at $E_\perp = 200$ meV would result in a dramatic reduction in the rate of water production and incomplete reaction. This was not observed, and once reaction took place it always went to completion. Similarly, a reduction of the barrier height as θ_{oxygen} decreases should result in an increase in rate superimposed on the Langmuir–Hinshelwood kinetics of the surface reaction. The fundamental shape of the reaction kinetic curve (figure 1) was insensitive to $E_\perp$ once reaction took place, even with $E_\perp$ just at the barrier value where the greatest distortions should take place. The insensitivity of the barrier to θ_{oxygen} is further demonstrated by the fact that the shape and position of the barrier indicated by the maximum reaction rate (figure 1) is independent of θ_{oxygen} [8]. Finally, we have recently re-measured the dissociative barrier of H_2 on Cu(110) at $T_s = 140$ K and obtain a value of 200 meV [9], in agreement with the apparent barrier in the oxygen reaction (figure 1).

The rate of the reaction, once the dissociative barrier had been overcome, was measured (starting the reaction at $\theta_{oxygen} = 0.5$) as a function of T_s in an attempt to estimate the activation energy in the new rate-determining step on the surface. Arrhenius plots for the reaction rate at various θ_{oxygen} were obtained from the temperature dependence in the range 650–800 K (e.g. $\theta_{oxygen} = 0.3$: see inset in figure 2). A plot of the activation energy ΔE for the surface process is plotted in figure 2 and demonstrates a clear dependence on θ_{oxygen}. The data also suggest that $\Delta E \rightarrow 0$ linearly as $\theta_{oxygen} \rightarrow 0$. The extrapolated value at $\theta = 0.5$ of $\Delta E = 600$ meV lower than the coverage-independent value obtained previously ($\Delta E = 850$ meV) [2]. A value of $\Delta E = 300$ meV is associated with the reaction of H_a and O_a to produce water in the same reaction on Pd(111) [10], and (despite the differences in ΔE) the same rate-determining step was suggested for Cu(110) [2, 3]. It is tempting to extend this conclusion to Cu(110), on the basis of very similar activation energies and reaction rates obtained here for Cu(110) to those obtained for Pd(111) [10]. However, it is difficult to rationalise the strong oxygen
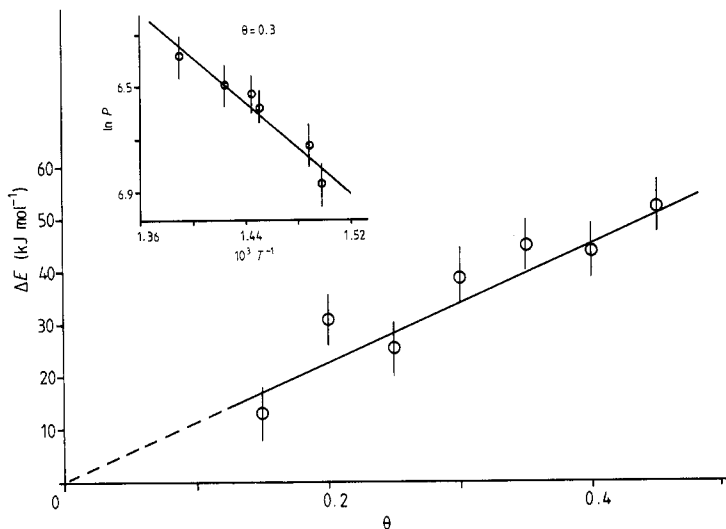
Figure 2. The activation energy ΔE for the surface rate-determining step following H_2 dissociation. ΔE has been obtained from Arrhenius plots (inset) at constant θ_{oxygen}. $E_\perp$ = 250 meV.

coverage dependence for this step. Conceivably lateral interactions between oxygen atoms could influence the surface reaction, but it seems to us premature to speculate at this juncture how θ_{oxygen} influence ΔE until we are confident about the new rate-determining step. For example, it appears that the movement of sub-surface hydrogen into the surface layer on Pd(111) [10] plays an important role in the surface reduction kinetics. It is possible that such a process would be sensitive to θ_{oxygen} and may well be important on Cu(110) where there is evidence that sub-surface hydrogen stabilises the (1×2) reconstruction [11]. Unfortunately the system is further complicated by the induced reconstruction of the oxygen in the (2×1) overlayer [6, 7].

It is interesting to note that the reaction probability obtained here for water production once the hydrogen dissociation barrier is not rate limiting is very similar to the probability of HD production, which exhibited no surface activation barrier [4] at low deuterium coverages. We also note that if our barrier for H_2 dissociation of 200 meV is used to interpret the earlier results using a thermal source, we predict the significantly reduced reaction probability $(10^{-7}\text{--}10^{-5})$ observed [2] in the same temperature regions. In doing so we can rationalise the apparent discrepancy between that result and similar surface reductions [2, 3, 4, 9] where no dissociative adsorption barrier exists.

4. Conclusion

The reaction of hydrogen with a Cu(100)–(2 × 1) oxygen overlayer exhibits kinetics consistent with the Langmuir–Hinshelwood scheme, and the rate-determining step for a thermal H_2 source will be the dissociative adsorption of H_2. The rate of water production was undetectably low for hydrogen beam energies $E_\perp < 200$ meV, but increased sharply at $E_\perp \geqslant 200$ meV. The sharp increase in the rate of water production is dependent on the normal component of hydrogen translational energy. This change in kinetics is associated with an apparent activation barrier in the entrance channel to dissociative

hydrogen adsorption, which is placed at $E \geqslant 200$ meV. The barrier is insensitive to oxygen coverage and, although somewhat higher than that obtained previously on a clean surface [4], it corresponds closely to that measured on the same Cu(110) crystal surface at 140 K [9]. Once the dissociative barrier has been overcome at $E_{\perp} \geqslant 200$ meV, the surface temperature dependence of the reaction allows us to estimate an activation energy associated with the new rate-determining step $\Delta E \simeq 600$ meV at $\theta = 0.5$, which reduces to zero as $\theta_{\text{oxygen}} \to 0$.

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