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The Oxidative Dehydrogenation of Methanol at the CuPd[85 : 15]{110} $p(2 \times 1)$ and Cu{110} Surfaces: Effects of Alloying on Reactivity and Reaction Pathways

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The adsorption and selective oxidation of methanol to formaldehyde over CuPd[85 : 15]{110}$p(2 \times 1)$ and Cu{110} has been investigated using a thermal molecular beam. Methanol oxidation on the alloy surface appears, at first sight, to be very similar to that seen on Cu{110}: the shapes of the methanol sticking curves and product evolution curves are very similar to those seen on Cu{110}. It is found, however, that temperature dependence of the sticking coefficient for methanol varies in a manner opposite that seen for Cu{110}; at temperatures below ∼400 K the reaction stoichiometry is consistently lower than seen for Cu{110}; above 400 K in the 1/4ML O/CuPd[85 : 15]{110}$p(2 \times 1)$ case this stoichiometry is seen to increase with temperature. Preoxidation of the surface to 1/2ML oxygen coverage results in behaviour that is more Cu like with no obvious increase in reaction stoichiometry at high (>400 K) temperature; in this case an increase in the net stoichiometry of reaction only occurs at lower surface temperatures.

In both 1/4ML and 1/2ML cases the rate of reaction of methanol is found to be faster on the alloy surface than on Cu{110}.

The above differences in behaviour are rationalised in terms of an alloy-induced destabilisation of the surface methoxy species of around 2.5 kJ mol^{-1} and a thermally induced Pd segregation during beam reactions conducted at above ∼400 K. The apparent differences in behaviour between the 1/4ML and 1/2ML O cases on the alloy surface are also discussed in terms of the microscopic manner in which the methanol oxidation reaction is known to proceed on Cu{110}.

Key Words: **methanol oxidation; copper; alloy surface; molecular beams; reaction mechanisms.**

INTRODUCTION

The possibility that supported metal catalysts, composed of more than one metallic component alloyed with another, may give rise to novel and useful chemical or physical properties has been demonstrated for a number of heterogeneous catalytic systems (1). This promise continues to be the driving force for studies into mixed metal systems at all levels, from complete catalysts to single crystals. Catalysts based on Cu mediate a number of related reactions including methanol synthesis (2) and methanol oxidation to formaldehyde (3). In these processes common intermediates are found: adsorbed formate ($HCOO_a$) and adsorbed methoxy (CH_3O_a). Both have varying degrees of importance in the overall reaction scheme: whilst it is thought to be the pivotal intermediate in methanol synthesis, $HCOO_a$ could be regarded as deleterious in the methanol oxidation process, as formation of this species is likely to lead to complete combustion of the methanol rather than selective conversion to formaldehyde (H_2CO). Thus, in considering the modification of a copper catalyst through, for instance, alloying with Pd, we would ideally like to know how this affects the interplay and interconversion between these important surface intermediates.

The CuPd[85 : 15]{110} surface has been studied by a number of groups (4–7, 9–13, 15, 30). Below ∼600 K this surface shows a $p(2 \times 1)$ symmetry (4–6); this symmetry arises from an ordered second layer of Pd of stoichiometry CuPd. The surface layer itself is depleted in Pd; the degree of depletion is, however, open to some question. On the basis of the relative strengths of the CuCu, CuPd, and PdPd bonds, and surface free energy terms the equilibrium surface layer is predicted to be essentially devoid of Pd (7). The surface bilayer therefore approximates to the ordered $\alpha'(Cu_3Pd)$ phase predicted from the bulk phase diagram (8); the "ideal" Pd free {110} termination of this bulk structure is shown in Fig. 1 and represents the working model that we have for the $p(2 \times 1)$ alloy surface. However, though this model adequately fits angle dependent XPS and qualitative LEIS (1 KeV He) (6) measurements, subsequent studies using LEIS (2 KeV Ne) have arrived at a figure of 5–10% Pd in the surface layer (9, 10).

Thermal decomposition of adsorbed formate from this surface indicates that the formate is uniformly destabilised

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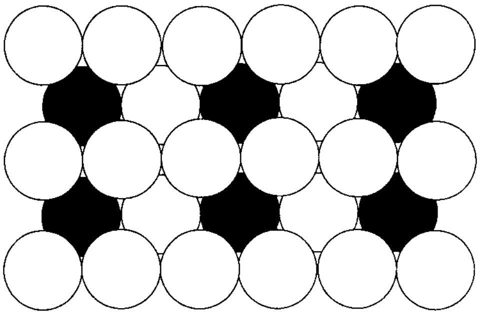

FIG. 1. The CuPd[85 : 15]{110}$p(2\times1)$ surface. Open circles, Cu; filled circles, Pd. The model shown is that deduced from (5–7) and is equivalent to the Cu-terminated {110} truncation of the bulk α' Cu_3Pd phase (8).

relative to Cu{110} with respect to dehydrogenation by around 7–10 kJ mol^{-1} (6); there is no evidence for separate decomposition sites due to surface Pd.

Importantly, for the current case, core level X-ray photoelectron diffraction (11, 12) shows that, upon adsorption of oxygen, the alloy surface reconstructs in essentially the same way as Cu{110}. It has also been shown (13) that the process of oxygen adsorption itself appears unperturbed by the presence of Pd in the surface region; the magnitude of the initial sticking probability (S_0), the coverage dependence of the sticking coefficient, and the apparent activation energy for this process are the same, within experimental error, as found for Cu{110} (14).

A supersonic beam investigation of H_2 dissociation on the $p(2\times1)$ alloy surface (15) showed the sticking probability for this process to be lower than that for Cu{110}. However, on the metastable (1×1) surface that this alloy produces upon sputtering at low temperature, the sticking was significantly greater than for Cu{110}, and a Pd-like TPD feature indicated the presence of small islands of Pd at the surface. The (1×1) surface contains surface Pd at approximately the concentration of the bulk (~15%) (6).

Methanol oxidation over Cu-based catalysts has been the subject of much surface science research over the past 20 years (16–27). However, there remains a degree of conflict regarding various aspects of the conversion of methanol to formaldehyde over oxidised Cu surfaces, most notably in the overall reaction stoichiometry at low temperature and the efficacy of formate ($HCOO_a$) synthesis during this process. However, scanning tunnelling microscopy (STM) experiments (16–18) have revealed in detail how this reaction proceeds, in a spatial sense, on Cu{110}.

The results of a number of investigations have derived the following reactions occurring on Cu{110}:

$$CH_3OH + O_a \rightarrow CH_3O_a + OH_a \qquad [1]$$

$$CH_3OH + OH_a \rightarrow CH_3O_a + H_2O_a \qquad [2]$$

$$CH_3O_a + OH_a \rightarrow CH_2O_a + H_2O_a \qquad [3]$$

$$CH_3O_a \rightarrow CH_2O_a + H_a \qquad [4]$$

$$CH_2O_a \rightarrow CH_2O_g \qquad [5]$$

$$H_2O_a \rightarrow H_2O_g \qquad [6]$$

$$2H_a \rightarrow H_{2g} \qquad [7]$$

$$CH_3O_a + H_a \rightarrow CH_3OH_g. \qquad [8]$$

On the clean Cu{110} surface there is no net formation of the methoxy species due to the difficult nature of the dissociation process, the facile nature of step [8], and the relatively high barrier to H_a recombination on Cu{110} (step [7]).

At room temperature step [6] is facile and methoxy decomposition (step [3]) is very slow. Thus, the uptake methanol by the Cu surface, and the consequent production of H_2O and CH_3O_a, is dominated by steps [1] and [2]. It can be seen that in the limiting case of a stable methoxy species, the observed methanol uptake stoichiometry will be $2CH_3OH : 1O_a$. In this case the only source of H_a for the formation of water is the methanol hydroxyl group; this has been demonstrated through the use of isotopically labelled methanol (22).

A second limiting case arises at higher reaction temperatures when step [3] has become far faster than step [2]. In this case an incoming methanol molecule is dehydrogenated at the hydroxyl group (step [1]) but, before a second methanol molecule can arrive at the reaction site, the first dehydrogenates to form water and adsorbed formaldehyde, both of which desorb rapidly. It is evident that, in such a case, the net reaction stoichiometry must be $1CH_3OH : 1O_a$.

We can therefore see the reaction stoichiometry on Cu{110} as arising out of a relatively simple competition between these two cases. The only complication factor here is step [7]. Where unimolecular methoxy decomposition occurs to any great degree on areas of clean Cu then the adsorbed hydrogen released has three options open; it may be trapped by either O_a or OH_a, it may recombine with the adsorbed methoxy species to reform gas phase methanol, or it may find another adsorbed hydrogen atom and combine to give H_{2g}. If the latter occurs it necessarily means that, in order to remove all the oxygen from the surface, more methanol molecules will have to be adsorbed and reacted. In the Cu{110} case the relative barriers to methoxy decomposition (step [3]) and methanol formation (from step [8]), and the barrier to hydrogen recombination (step [7]), mean that this is a minor pathway being seen only over a relatively small temperature range before the reaction is completely dominated by steps [1] and [3]. On Cu{110} the reaction stoichiometry is therefore seen to decrease from ~2 : 1 to 1 : 1 relatively smoothly as the surface temperature is increased (17, 22).

Much the same has been concluded for this reaction on Cu{111} using another, related, beam technique (23, 24).

However, reports exist (25, 26) that claim a reaction stoichiometry of 1 $CH_3OH : 1O_a$ even at room temperature; these reports are based on XPS and thermal desorption measurements alone.

Alongside stoichiometry a further reaction has also been the source of some disagreement: that of the synthesis of adsorbed formate, i.e.,

$$CH_2O_a + O_a \rightarrow CH_2OO_a \quad [9]$$

$$CH_2O_{2a} \rightarrow HCOO_a. \quad [10]$$

Reactions [9] and [10] are known to be facile on Cu{110}, formate being seen in TPD from formaldehyde adsorbed at partially oxidised Cu{110} (28). As formaldehyde desorbs at very low temperature (~200 K) on Cu{110} the implication is that, in the presence of adsorbed oxygen, there is a high probability for formate synthesis providing the residence time of the formaldehyde is appreciable and it is not lost to the gas phase via step [5].

In some early papers (19, 20) formate synthesis, during TPD from methanol adsorbed on partially oxidised Cu{110}, was indeed seen; repetition of these experiments within the same group, however, failed to reproduce this (21). Later work, using a molecular beam (22), reinforced the latter view. We have previously demonstrated (30) that significant levels of formate can be made during methanol oxidation carried out in the same manner as those in (22), implying a difference in behaviour between the alloy and pure Cu surfaces.

Alongside this there have also been other reports of formate synthesis during methanol oxidation on Cu{111} (23, 24) and Cu{110} (25, 26), but not on Cu{100} (27). Indeed, recent TPD measurements have shown that this route can be significant on oxidised Cu{110} surfaces under certain conditions (31).

EXPERIMENTAL

The experiments were performed in two similar stainless steel UHV chambers. The experiments on the alloy surface were performed in a system previously described (32). Measurements on Cu{110} were performed in a similar beam chamber described in detail more recently (33). Both systems were equipped with LEED and Auger facilities to allow assessment of surface cleanliness and surface order.

The experiments on the alloy surfaces were made with a beam of 2.9 mm diameter and flux of $\sim 2 \times 10^{13}$ molecules/cm^2/sec (for O_2 at pressure of 10 Torr behind beam). The beam used for the experiments on Cu{110} had a diameter of 7 mm and a flux of $\sim 1.3 \times 10^{13}$ molecules/cm^2/sec (14 Torr O_2 behind beam). The methanol beam experiments, in the first case, 10 Torr behind the beam source, and, in the second case (for Cu{110}), 20 Torr. Thus the net beam fluxes used in each case were very similar (1.9–2 $\times 10^{13}$ molecules cm^{-2} s^{-1}); as such the result of each set of experiments should be readily comparable. The sticking probabilities for methanol and oxygen were measured using the King–Wells method (34) and all the methanol oxidation experiments were conducted with the beam source at room temperature.

The preparation and mounting of the respective samples and of the gases used has been detailed elsewhere (7, 17, 30). In both cases the sample temperature was measured using a chromel–alumel thermocouple inserted into a spark-eroded hole in the side of the single crystals.

Reactant uptake and product evolution from the reaction in the beam, and gas evolution in subsequent TPD measurements, was made using multiplexed quadropole mass spectrometers.

RESULTS AND DISCUSSION

1. *Methanol Oxidation*

1.1. Clean surfaces. Though not shown here, beams of methanol were exposed to clean Cu{110} and CuPd[85 : 15]{110}$p(2 \times 1)$ surfaces at room temperature; in both cases there was no net uptake of methanol from the beam and no subsequent desorption from either surface in TPD. Neither clean surface shows any observable activity for formaldehyde production, in the absence of oxygen, at room temperature.

1.2. Oxygen precovered surfaces. Methanol oxidation was carried out at oxygen coverages of 1/4ML and 1/2ML. In this notation 1/2ML represents the oxygen coverage wherein the whole of a Cu{110} surface is reconstructed to the $p(2 \times 1)$ missing row reconstruction and LEED shows a sharp $p(2 \times 1)$ structure. 1/4ML coverage is therefore the situation where half the surface area of the substrate is reconstructed and the other half remains oxygen free; in this case the LEED shows streaking in the {001} direction.

2. *Methanol Oxidation at 1/4ML Oxygen Coverage*

2.1. Methanol uptake and product evolution. Figures 2a and 2b show the sticking probability (S_{met}) for CH_3OH, on the 1/4ML oxidised alloy and Cu{110} surfaces, as a function of coverage and of surface temperature. Over the temperature range investigated the general shape of the sticking curves is similar in both cases. Substitution of CD_3OD for CH_3OH in these experiments results in no significant differences in the temperature range investigated.

However, the 1/4ML O/Cu{110} surface shows consistently lower values of S_{met} over the temperature range. This disparity is at a minimum at lower reaction temperatures (340–360 K) but grows rapidly due to the inverse behaviour of S_{met} with T (K) between the two surfaces. The differences in the total amount of methanol consumed during an experiment, as a function of surface temperature, are shown in more detail in Fig. 3.

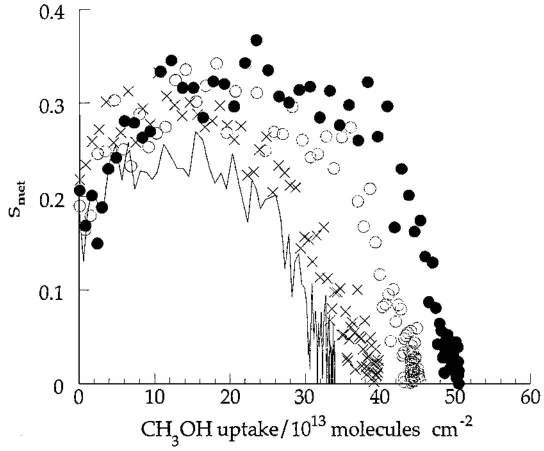

FIG. 2a. Sticking probability versus uptake curves for CH_3OH uptake at the 1/4ML O-predosed CuPd[85 : 15]{110}$p(2 \times 1)$ surface for a range of surface temperatures: line, 341 K; crosses, 362 K; open circles, 402 K; filled circles, 431 K.

It can be seen that, though the overall nature of the reaction (from the shape of the uptake curves) has been conserved in going from the elemental to the alloy surface, there are considerable differences between the two surfaces: on the alloy surface the high-temperature reaction stoichiometry is higher than that seen for Cu{110}; at low temperatures the reverse is true. Though the errors expected from integrating S_{met} with time are quite large they do not explain the difference in stoichiometry observed at either end of the temperature range.

Figure 4 shows plots similar to those of Fig. 3 but shows temperature dependent yield of various products being evolved during the reaction itself and/or in postreaction TPD: the corresponding data for the reaction of CH_3OH on the equivalent Cu{110} surface can be found in (17).

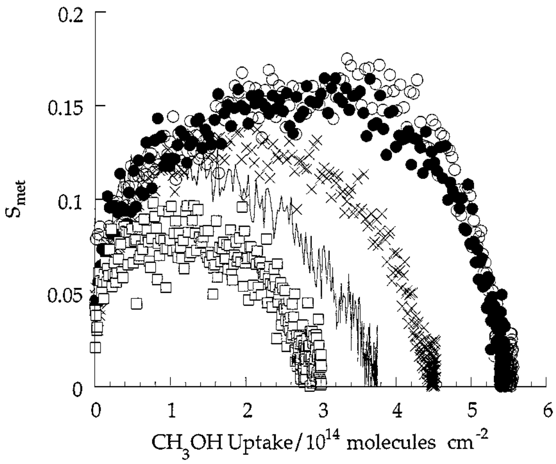

FIG. 2b. The same as Fig. 2a but for CH_3OH adsorption at the 1/4MLO/Cu{110} surface. The surface temperatures are as follows: open circles, 353 K; filled circles, 373 K; crosses, 393 K; line, 453 K; open squares, 523 K.

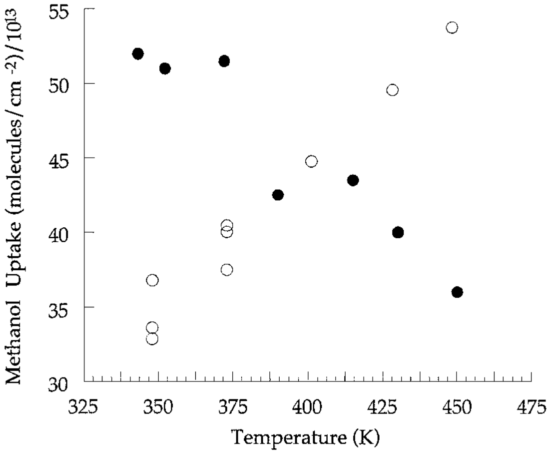

FIG. 3. Reaction stoichiometry (calculated from methanol uptake curves; see text) versus reaction temperature for methanol oxidation at the 1/4ML preoxidised Cu{110} (filled circles) and alloy $p(2 \times 1)$ (open circles) surfaces.

These figures show data recorded down to reaction temperatures of ~300 K. The absence of such data for the preceding uptake figures (based solely on the determination of methanol sticking) is due to the difficulty in determining S_{met} (and hence uptake) on the alloy surface at temperatures much below 350 K. Again substitution of CD_3OD for CH_3OH produces no substantial differences in behaviour; however, better data were obtained in product evolution using CD_3OD (especially for $H_2(D_2)$ and $H(D)_2O$), and thus this has been used here.

Above ~400 K there is a marked increase in hydrogen and formaldehyde production, in keeping with the uptake data shown in Figs. 2 and 3.

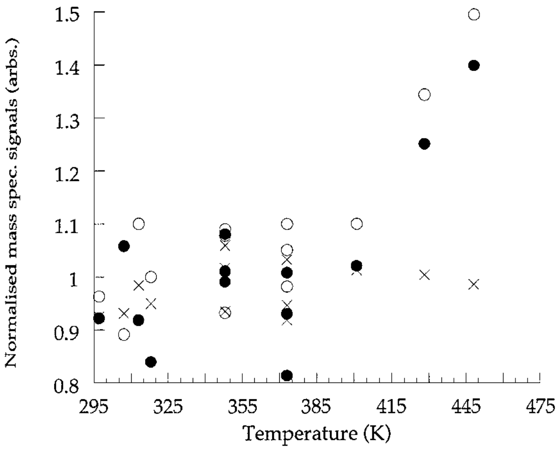

FIG. 4. Normalised product evolution, as a function of temperature, during CD_3OD oxidation at the 1/4ML O-predosed CuPd[85 : 15]{110}$p(2 \times 1)$ surface. Full circles, CD_2O; open circles, D_2; crosses, D_2O. Each point is the sum of products evolved during the beam reaction and those produced in subsequent TPD experiments. The corresponding data for Cu{110} can be found in (17).

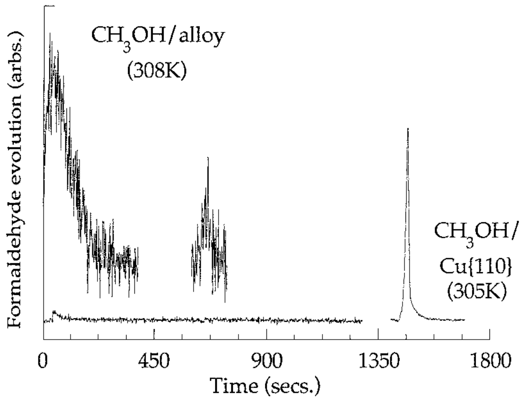

FIG. 5a. Temporal formaldehyde evolution during the beaming of methanol to both 1/4MLO alloy and Cu surfaces and in subsequent thermal desorption experiments. The legends define the system each trace corresponds to. The reaction temperatures are as follows: CH_3OH/alloy, 308 K; CH_3OH/Cu{110}, 305 K. The traces from each surface have been normalised to fit on the same scale and have been offset for clarity.

2.2. Rates of reaction on the 1/4ML oxygen predosed alloy and Cu{110} surfaces and stability of the surface methoxy species. Figure 5a shows a comparison of formaldehyde evolution from exposure of the 1/4ML O alloy and 1/4ML O–Cu{110} surfaces to methanol at ~308 and 305 K, respectively. In each case the trace beginning at $t = 0$ shows evolution during the beam reaction; the second trace is derived from a subsequent TPD experiment. In this case we are interested in the relative amounts of product released to the gas phase during and after the beam experiment.

On the alloy most of the methanol adsorbed during the beam experiment (~92%) reacted within the timescale of the beam experiment; only a tiny fraction (~8%) remains to be reacted away in the TPD. On Cu{110} the vast majority of the adsorbed methanol (~92%) remains on the surface as adsorbed methoxy during the beam experiment; only a small fraction is released during this time. Though not shown here, CD_3OD reacting on the alloy surface (at 308 K) shows an intermediate situation wherein ~20% of the adsorbed methoxy species is stable during the experiment.

Alongside these measurements it should be noted that no LEED pattern, other than the $p(2 \times 1)$ characteristic of both clean and oxidised alloy surfaces, was observed after any experiment; after the beam experiment on Cu{110} shown in Fig. 5a, LEED showed a (5×2) structure characteristic of a high level of adsorbed methoxy (17).

Figure 5b again shows formaldehyde evolution (at ~455 K) from differing beam reactions (as indicated). At this elevated temperature postreaction TPD shows no desorbing species and is therefore omitted. This graph is designed to show only the temporal differences in product evolution between the differing cases investigated.

As was mentioned earlier the fluxes of the two beams used are very similar, and therefore the data for the alloy and Cu{110} should be directly comparable. Note should, however, be taken of the considerable differences in methanol turnover in each reaction (Fig. 3).

It can firstly be seen that over the temperature region there is a small kinetic isotope effect (KIE) in the methanol oxidation reaction on the alloy surface; further, we can also see that the reaction for CH_3OH on the alloy at 455 K surface goes to completion more quickly than is the case for the same reaction on the partially oxidised Cu{110} surface (at 455 K). Clearly, there are distinct differences between the rates of reaction on each surface.

The conclusion from the above is that the methoxy species formed on the alloy surface is less stable toward dehydrogenation to formaldehyde than its counterpart on Cu{110}; this is clearly indicated in Fig. 5a. The presence of Pd in the selvedge region has made this surface more active toward this dehydrogenation reaction, in a manner similar to that seen for the formate intermediate on the CuPd[85 : 15]{110}$p(2 \times 1)$ surface (6, 12).

This observation allows us to rationalise the lower stoichiometry of reaction at low reaction temperatures seen on the alloy surface. In the reaction scheme outlined in the Introduction the overall reaction stoichiometry is principally determined by a competition between steps [1]–[3]. If a molecule adsorbed in step [1] can dehydrogenate via step [3] before a second molecule can arrive at the surface and remove O_a as water the overall stoichiometry of the reaction tends toward $1CH_3OH : 1O_a$; if the reverse is true the stoichiometry tends to 2 : 1. If at a given temperature, say 310 K, the methoxy dehydrogenation step is still active (as in the alloy case) then some of the oxygen at the surface will be lost through a 1 : 1 interaction of the methanol with the oxygen, and the net stoichiometry of the reaction will be lowered with respect to a situation (as in the Cu{110} case) where the methoxy species is essentially stable and

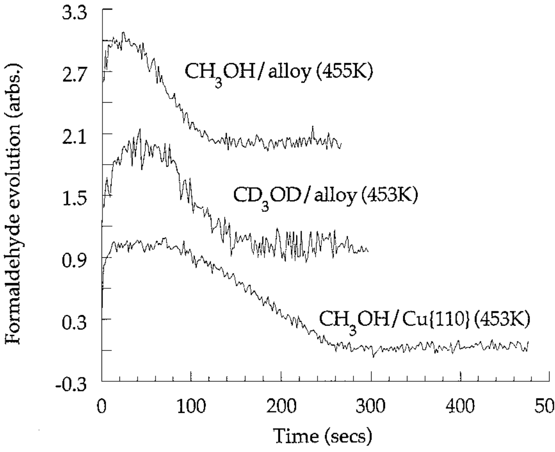

FIG. 5b. The same as Fig. 5a but with the following reaction temperatures: CH_3OH/alloy, 455 K; CD_3OD/alloy, 453 K; CH_3OH/Cu{110}, 453 K. In this case postreaction TPD experiments showed no product evolution and are therefore omitted.

the removal of oxygen as water can only occur through deprotonation of the methanol molecule at its hydroxyl group.

Can we, however, make an estimate of the magnitude of the destabilisation of the CH_3O_a species on the alloy, relative to Cu{110}? In the absence of detailed reaction modelling, which is considered to be beyond the scope of the current paper, the best we can do is to invoke a number of assumptions and test the simplest hypothesis that the rate of formaldehyde evolution is simply proportional to the rate constant for step [3] (methoxy decomposition to produce formaldehyde),

$$d(\mathrm{CH_2O_g})/dt \alpha \nu_{\mathrm{d}} e^{-E_{\mathrm{d}}/RT}, \qquad [11]$$

where ν_{d} denotes the pre-exponential factor for methoxy dehydrogenation, E_{d} the associated activation energy, and T the sample temperature. From the uptake data (Fig. 3) we know how much methanol is being reacted in each case, and we know the length of time this takes from the type of data shown in Fig. 5. In addition we know that the beam fluxes in each case are similar. If we simply take average rates of formaldehyde production (number of methanol molecules converted/time for reaction to complete) and assume that the pre-exponential factors are invariant between systems, then we can derive apparent differences in the activation energies for the methanol oxidation reaction (ΔE_{d}). By comparing data from a number of similar experimental runs over the temperature range ~300–450 K we obtain using this approach ΔE_{d} (Cu{110}–CuPd{110}) ~2.8 (±0.5) kJ mol^{-1}.

3. Methanol Oxidation at 1/2ML Oxygen Coverage

3.1. Methanol uptake and product evolution. Figure 6 shows the variation of S_{met} for beam reactions performed on the alloy surface at 1/2ML oxygen precoverage. Initially S_{met} is found to be very low—below the detection limit of the measurement technique. A reaction is, however, proceeding at some level and the sticking probability increases through a maximum before dying away again as the reaction goes to completion. Again the overall shape of the sticking curves is similar to that observed for the reaction on Cu{110} (17). However, there is only a very slight dependence of the total uptake with temperature compared to the 1/4ML case (Figs. 4 and 5).

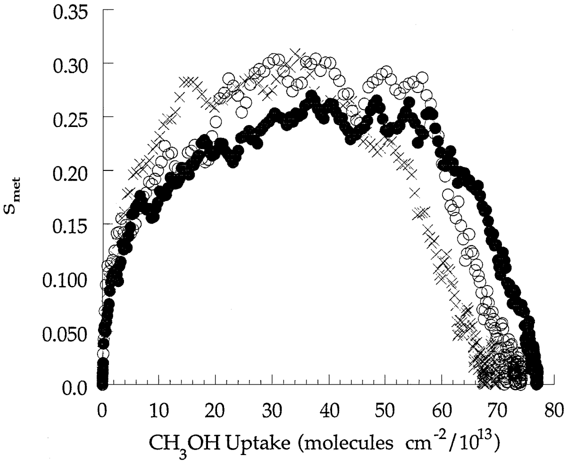

FIG. 6. Variation in sticking probability with methanol uptake for the reaction of CH_3OH at the 1/2ML oxidised CuPd[85 : 15]{110}$p(2 \times 1)$ surface. The reaction temperatures in each case are as follows: solid circles, 348 K; open circles, 398 K; crosses, 436 K.

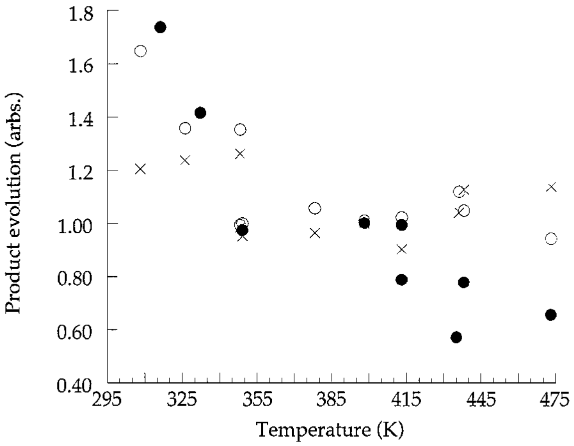

FIG. 7. Variation in gas phase product evolution with temperature for CD_3OD reacting at the 1/2MLO/alloy surface. Filled circles, D_2; open circles, D_2CO; crosses, D_2O.

Figure 7 shows the variation of product evolution with temperature. All the data shown have been normalised to reaction at ~400 K. We can see that above 350 K formaldehyde production appears relatively constant. However, below 350 K, where the sticking of methanol becomes very difficult to measure, we can see that, far from staying constant, the level of methanol uptake has increased. Indeed, the overall shape of the product evolution curve is far more like that seen for this reaction on Cu{110} (17) save for that it has been shifted to lower temperature.

Thus it would seem that, on top of the poisoning effect high levels of oxygen predosing have on the methanol oxidation reaction, the adsorbed oxygen has in some way caused the temperature dependence of the stoichiometry to adopt characteristics more like Cu{110}.

The upturn in reaction stoichiometry at low reaction temperatures is qualitatively what we would expect to occur in this system; sooner or later the methoxy species, even on the alloy surface, must become stable, and the reaction stoichiometry must tend toward 2 : 1 (see the Introduction). However, we saw no such upturn in the 1/4ML experiments at similar temperatures; there would therefore appear to be another factor involved.

3.2. Rates of reaction on the 1/2ML oxygen-predosed alloy and Cu{110} surfaces. Figure 8 shows a comparison of

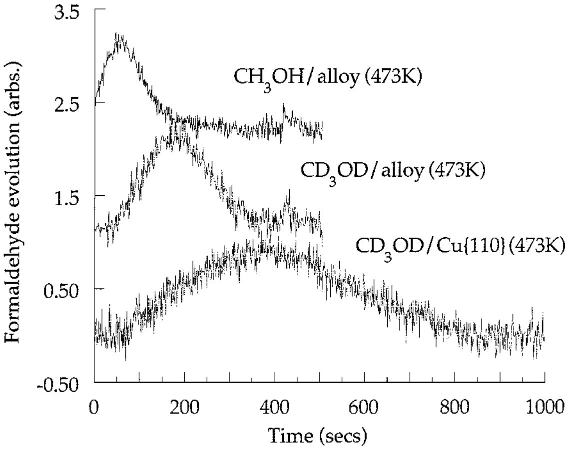

FIG. 8. Comparison of the rates of reaction of CH_3OH and CD_3OD at the 1/2MLO precovered alloy surface, and that observed for the reaction of CD_3OD on the equivalent Cu{110} surface, at 473 K.

the rates of reaction at 473 K for two systems: CD_3OD on 1/2ML-predosed Cu{110} and alloy surfaces, and CH_3OH on the alloy surface. Once again we can clearly see that the reaction goes to completion much more quickly on the alloy surface compared to Cu{110}.

Application of the assumptions made for the rates of reaction in the 1/4ML case to the 1/2ML experiment at 473 K yield a difference in the apparent activation energy (ΔE_d) for the methanol oxidation process, between the CH_3OH/Cu{110} and the CD_3OD/alloy reactions, of ~6.6–7 kJ mol^{-1}. The known KIE between the decomposition of CH_3OH and CD_3OD on Cu{110} is ~4.6 (± 1) kJ mol^{-1} (35). Thus in this case we are measuring both the difference in apparent reactivity between the elemental and alloy surfaces, and the KIE in the methoxy dehydrogenation on Cu{110}. Subtraction of the KIE value derived in (35) from the apparent activation energy gives 2–2.4 kJ mol^{-1} for the differential between CH_3OH reacting on the alloy and Cu{110} at 473 K; this range of values is consistent with that derived above for the 1/4ML reaction and would seem to indicate that the assumptions made in this respect are reasonable in this temperature region.

4. *Rationalisation of Observations*

Figure 5a provides the most direct evidence that the methoxy intermediate is less stable on the alloy surface than it is on Cu{110}. We have already used this observation to qualitatively explain the low reaction stoichiometries observed at both 1/4ML and 1/2ML oxygen precoverages. We have also attempted to directly compare the rates of reaction in the various cases studied; this has implied that the methoxy species destabilisation on the alloy surface relative to Cu{110}, is of the order of 2.5 kJ mol^{-1}.

The stability of the methoxy intermediate could also have some determining effect on the values of, and trends in, S_{met} observed in the systems we have investigated. However, a number of these changes could be explained through dynamic factors occurring in the methanol chemisorption step. If a barrier to the formation of the methoxy species, from the methanol precursor, is present on the alloy surface, the increase in S_{met} with surface temperature could be qualitatively explained.

If there were a barrier above the energy zero for the system, in the adsorption step to form methoxy, then we would expect there to be a temperature dependence in S^0_{met} of the form (36)

$$S^0_{\text{met}} = [1 + \nu_d/\nu_a e^{-(E_d - E_a)/kT}]^{-1}, \qquad [12]$$

where ν_d/ν_a is the ratio of the pre-exponential factors for desorption and adsorption from the precursor, respectively; k is the Boltzman constant; and $E_d - E_a$ is the difference in the barrier height for adsorption and desorption from the precursor state. For adsorption to be activated from the precursor state, $E_a > E_d$ and therefore S^0_{met} should increase with temperature. From [12], however, the temperature dependence of S is weak and would lead to a relatively small (10–15%) increase in the sticking coefficient over a 100 K temperature range (for a 2–3 kJ mol^{-1} barrier to methoxy formation). If we consider the effect at S^0 we can see that such an effect is below the experimental error of the sticking measurement; further, in considering the variation of S at other coverages it is clear that the changes we observe in the 1/4ML case are much larger than this. Thus, though we cannot rule this possibility out on the basis of the current measurements, such an effect would be relatively insignificant in terms of the changes in S_{met} that we are observing in the 1/4ML case as the reaction temperature is increased.

A destabilisation of the methoxy will result in a lower steady-state concentration of this species at the surface. This results in a higher concentration of sites active for adsorption at the surface and, at the same time, reduces the possibility of methoxy species recombining with H_a to form gas phase methanol; a higher S_{met} will therefore result through reduction of self-poisoning in methanol adsorption. Thus at relatively low reaction temperatures we can qualitatively explain the trend in absolute sticking coefficients through the relative stability of the methoxy species involved, i.e.,

$$CH_3OH(\text{alloy}) < CD_3OD(\text{alloy}) < CH_3OH(\text{Cu}\{110\}).$$

This explanation may go some way in rationalising the low-temperature data from the alloy. On its own, however, it will not explain why above 400 K, in 1/4ML situation, the sticking probability (and reaction stoichiometry) is seen to rise. From the mechanisms outlined in the Introduction, which we have no reason to doubt are valid for the alloy, the reverse should be observed; if all the other steps were unmodified relative to Cu{110}, a less stable methoxy species would cause the stoichiometry to fall even more rapidly to 1 : 1 with increasing temperature.

The only other step that directly affects the overall reaction stoichiometry is step [7], hydrogen recombination. If hydrogen recombination could be promoted in some way, or if the hydrogen produced in the surface reactions could be prevented from reacting with adsorbed oxygen, then an increase in overall stoichiometry would result.

Such effects would also allow step [7] to compete with recombination (step [8]) to form methanol from H_a and CH_3O_a; step [8] provides a route for effectively diminishing the number of molecules observed to stick by this method. A lowering of the barrier to step [7], or the appearance of a new route to accommodate this step more efficiently, would provide a means to diminish the probability of recombinative methanol desorption and should cause the observed value of S_{met} to rise.

In a previous supersonic beam study on this alloy (15), it was observed that, though the $p(2 \times 1)$ surface showed an extremely low sticking probability for hydrogen adsorption ($<10^{-7}$), the disordered (1×1) surface of this alloy showed a much increased sticking coefficient ($>10^{-4}$). This study also provided evidence for the presence of small Pd clusters on the $\{1 \times 1\}$ surface from the appearance of Pd-like TPD states wherein D_a is stable to ~400 K. Both of these observations would appear to point to surface Pd as the root cause of the upturn in stoichiometry observed above 400 K. In the current case, however, there is no evidence of high-temperature hydrogen desorption from postreaction TPD experiments; above 360 K the only hydrogen evolution in TPD is due to residual formate made during the beam reaction (see Ref. (30)).

Further, the reactivity of Pd{110} toward the decomposition or oxidation of methanol is also different from that of Cu. On Pd{110} (37–39) methanol is decomposed to CO and H_2; on the oxidised surface the products are CO, CO_2, and H_2 due to facile oxidation of the CO. If Pd were to be present as surface clusters at the surface we might expect some changes in the net selectivity observed and possibly Pd-like reaction pathways appearing. Any appreciable level of Pd-like behaviour would result in a decrease in the levels of formaldehyde produced during the experiment, with a concomitant increase in H_2/D_2 production; hydrogen and formaldehyde production are observed to rise together as the temperature is increased. Therefore we conclude that, within the temperature range investigated, the tendency toward Pd-like behaviour in this alloy surface is minimal.

At present, therefore, though we can indicate that the source of this behaviour is the appearance of surface Pd at elevated reaction temperatures, we cannot say specifically how this modification in reactivity is being mediated in the absence of direct evidence of, for instance, Pd-like desorption states in TPD.

The “Cu-like” behaviour of the reaction stoichiometry for the 1/2ML preoxidation case also requires explanation. The atomic scale progression of this reaction on Cu{110} is highly anisotropic (16–18). Oxygen removal only occurs from the termination of strings of oxygen that characterise the $p(2 \times 1)$ oxygen adlayer. At high initial oxygen coverage this process therefore creates very narrow areas of clean surface behind the reaction front. This may be contrasted with the 1/4ML situation, where there are large areas of the surface free of oxygen from then start of the reaction. On average, therefore, over a large portion of the 1/2ML reaction, the islands of clean surface produced will be considerably narrower than those of the equivalent 1/4ML reaction.

If we suppose that relatively large areas of clean surface are required to allow significant Pd segregation at any given temperature, then, in a narrow island of clean surface, the oxygen at each side of the island may pin the surface composition due to the relatively high affinity that oxygen has for Cu. In the 1/4ML case this will not be significant, as right from the start most of the clean surface area will not be affected by any such preference. Hence, over much of the 1/2ML reaction the free surface being formed will have a significantly smaller Pd content than is the case for the 1/4ML reaction. This in turn means that any changes in reactivity that surface Pd may imbue (above 400 K for instance) will be curtailed and the surface would show more Cu-like properties; this is what is observed experimentally.

The unidimensional progress of the oxygen removal, and the narrow areas of clean surface that this would tend to create, will also affect the packing and diffusion of the adsorbed methoxy species. In the 1/4ML case a methoxy species formed at the surface can diffuse across large areas of clean surface; in the early stages of the 1/2ML reaction that possibility is severely restricted. If we suppose that the kinetics of the methoxy dehydrogenation step are dependent upon its immediate environment then we may explain the difference in the low-temperature stoichiometries seen in the 1/4ML and 1/2ML reactions. Firstly we may suppose that the dehydrogenation event to from formaldehyde and H_a requires either a clean surface site or a terminal oxygen at the end of a chain of oxygen atoms. We might then surmise that, in the early stages of the 1/2ML reaction, the dehydrogenation of the methoxy species is hindered, as most of the methoxy atoms on the surface will exist next to other methoxy atoms or next to oxygen atoms within adjacent oxygen chains. Consequently the rate of dehydrogenation of these methoxy molecules is curtailed due to lack of reactive sites. In this situation the only way more oxygen can be removed from the surface as water is through dehydrogenation of that small fraction that are adjacent to terminal oxygen species or through the percolation of protons lost in the initial adsorption step, through the methoxy islands to the terminal oxygen atoms. In the 1/4ML case there will be a relative excess of possible sites for methoxy dehydrogenation and large areas of clean surface for these species to diffuse into; dehydrogenation can therefore proceed relatively unhindered. The net result of these factors is that, at a given temperature, the competition between steps [1]–[3] is shifted in favour of steps [1] and [2] in the early stages of the 1/2ML reaction; a higher stoichiometry is therefore observed than in the equivalent 1/4ML reaction. As the surface temperature is lowered this effect is amplified.

The above allows us to explain, at least qualitatively, the observed differences in the reactions of the alloy surface at differing levels of preoxidation. The best evidence for these hypotheses comes from STM measurements of the same reaction on Cu{110} (16–18), which gives credence to a number of the assumptions made above: the unidimensional removal of oxygen from the surface (only terminal oxygen species are active) and the presence of clean surface affecting the kinetics of methoxy decomposition at low temperature (40). The possibility that high coverages of oxygen may hinder Pd segregation to the surface is, however, only based on the relative affinities of oxygen for Cu and Pd. It should be noted that O-induced segregation of one component of an alloy system has been reported for a number of alloy systems and in general the element seen to segregate is that forming the most stable oxide (41).

The destabilisation of the adsorbed methoxy species should have significant ramifications for the formation of surface formate during oxidation. Formate production should be more efficient on the alloy surface at low temperatures, as the rate of formaldehyde production (step [3]) is faster on the alloy surface. In the present experiment this leads to a higher probability of trapping by an adsorbed oxygen species before all the oxygen is removed as water through competing processes (steps [1] and [2]). Formate species have been detected in postbeam reaction TPD experiments on Cu{110} (17, 18) though the absolute levels produced, or the temperature dependence of this pathway, have not been accurately quantified; as such we cannot show for certain that the apparent destabilisation of the surface methoxy species on the alloy surface is carried through to more efficient formate production at low temperature.

CONCLUSIONS

It has been shown that the presence of Pd in the CuPd{110}[85 : 15]$p(2 \times 1)$ selvedge leads to subtle changes in chemistry that have complex ramifications for the manner in which methanol is oxidised on this surface relative to that seen for Cu{110}: these can be summarised as follows:

(a) Within the temperature range investigated the global mechanistics of the methanol oxidation reaction, and the dual role of oxygen as promoter and poison at differing coverages, are qualitatively the same as observed for Cu{110}. There is little evidence for Pd-like behaviour in methanol oxidation across the temperature range investigated.

(b) The stability of the pivotal methoxy intermediate has, however, been changed. The CuPd[85 : 15]{110}$p(2 \times 1)$ surface shows an increased activity toward the dehydrogenation of this species compared to Cu{110}; this change is small and the differential in activation energies for methoxy dehydrogenation on the two surfaces is estimated to be of the order of ~2.5 kJ mol^{-1}.

(c) At reaction temperatures above 400 K the reaction stoichiometry, and the sticking coefficient for methanol on the 1/4ML pre-oxidised alloy surface, are found to increase. The most likely underlying cause of this is the diffusion of Pd to the surface. This provides an effective route for the trapping and/or desorption (at $T > 400$ K) of adsorbed hydrogen which would otherwise recombine with adsorbed methoxy species or be lost as water through reaction with adsorbed oxygen.

(d) 1/2ML O coverage results in much more Cu-like behaviour. This is believed to be due to the microscopic manner in which the oxidation reaction occurs. This leads to the formation of areas of clean alloy surface that are fundamentally different in aspect, over much of the reaction, from those present when starting from 1/4ML oxygen coverage. This in turn affects methoxy dehydrogenation, resulting in an increasing stoichiometry of reaction at low temperature, and curtails segregation of Pd to the surface layer, leading to no upturn in reaction stoichiometry above 400 K; both observations are more in keeping with the known reactivity of Cu{110}.

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REFERENCES

1. For a pertinent example, see Besenbacher, F., Chorkendorff, I., Clausen, B. S., Hammer, B., Molenbroek, A. M., Norskov, J. K., and Stensgaard, I., *Science* **279**, 1913 (1998).
2. See, for instance, Chinchen, G., Denny, P., Jennings, R., Spencer, M., and Waugh, K., *Appl. Catal.* **36**, 1 (1988), and references therein.
3. See, for instance, Walker, J. F., *in* "Formaldehyde," p. 1. Reinhold, New York, 1964.
4. Holmes, D., King, D. A., and Barnes, C. J., *Surf. Sci.* **227**, 179 (1990).
5. Lindroos, M., Barnes, C. J., Bowker, M., and King, D. A., *in* "The Structure of Surfaces III" (S. Y. Tong, M. A. Van Hove, K. Takaynagi, and X. D. Xie, Eds.), p. 287, Springer Series in Surface Science, Vol. 24. Springer, Berlin, 1991.
6. Newton, M. A., Francis, S. M., Li, Y., Law, D., and Bowker, M., *Surf. Sci.* **259**, 45 (1991).
7. Newton, M. A., Francis, S. M., and Bowker M., *Surf. Sci.* **259**, 55 (1991).
8. See, for instance, Brandes, A. E., Ed., "Smithells Metals Reference Book," 6th ed. Butterworths, London, 1983; Hultgren, R., Desai, D., Hawkins, D. T., Gleiser, J., and Kelley, K. K., "Selected Values of the Thermodynamic Properties of Metal and Alloys," Am. Soc. Metals, Ohio, 1973.

9. Bergmans, R. H., Van der Grift, M., Denier van der Gon, A. W., van Welzniz, R. G., Brongersma, H. H., Francis, S. M., and Bowker, M., *Nucl. Instrum. Methods B* **85**, 435 (1994).
10. Bergmans, R. H., Van der Grift, M., Denier van der Gon, A. W., and Brongersma, H. H., *Surf. Sci.* **345**, 303 (1996).
11. Newton, M. A., Francis, S. M., and Bowker, M., *Phys. Rev. B* **45**, 9451 (1992).
12. Newton, M. A., Francis, S. M., and Bowker, M., *Surf. Sci.* **269/270**, 41 (1992).
13. Newton, M. A., and Bowker, M., *Surf. Sci.* **307–309**, 445 (1994).
14. Pudney, P., and Bowker, M., *Chem. Phys. Lett.* **171**, 373 (1990).
15. Cottrell, C., Bowker, M., Hodgson, A., and Worthy, G., *Surf. Sci.* **325**, 57 (1995).
16. Leibsle, F. M., Francis, S. M., Davis, R., Xiang, N., Haq, S., and Bowker, M., *Phys. Rev. Lett.* **72**, 2569 (1994).
17. Francis, S. M., Leibsle, F. M., Haq, S., Xiang, N., and Bowker, M., *Surf. Sci.* **315**, 284 (1994).
18. Leibsle, F. M., Francis, S. M., Haq, S., and Bowker, M., *Surf. Sci.* **318**, 46 (1994).
19. Wachs, I. E., and Madix, R. J., *J. Catal.* **53**, 208 (1978).
20. Wachs, I. E., and Madix, R. J., *Surf. Sci.* **76**, 531 (1978).
21. Bowker, M., and Madix, R. J., *Surf. Sci.* **95**, 190 (1980).
22. Barnes, C., Pudney, P. D. A., Guo, Q., and Bowker, M., *J. Chem. Soc. Faraday Trans.* **86**, 2693 (1990).
23. Gates, S. M., Russell, J. N., and Yates, J. T., *Surf. Sci.* **159**, 233 (1985).
24. Russell, J. N., Gates, S. M., and Yates, J. T., *Surf. Sci.* **163**, 516 (1985).
25. Carley, A. F., Owens, A. W., Rajumon, M. K., Roberts, M. W., and Jackson, S. D., *Catal. Lett.* **37**, 79 (1996).
26. Carley, A. F., Davies, P. R., Mariotti, G. G., and Read, S., *Surf. Sci. Lett.* **364**, L525 (1996).
27. Sexton, B. A., *Surf. Sci.* **88**, 299 (1979).
28. Wachs, I. E., and Madix, R. J., *Surf. Sci.* **84**, 375 (1979).
29. Bowker, M., and Madix, R. J., *Surf. Sci.* **102**, 542 (1981).
30. Newton, M. A., and Bowker, M., *Catal. Lett.* **21**, 139 (1993).
31. Davies, P. R., and Mariotti, G. G., *J. Phys. Chem.* **100**, 19975 (1996).
32. Bowker, M., Pudney, P. D. A., and Barnes, C. J., *J. Vac. Sci. Technol. A* **8**, 816 (1990).
33. Bowker, M., Rowbotham, E., Leibsle, F. M., and Haq, S., *Surf. Sci.* **349**, 97 (1996).
34. King, D. A., and Wells, M. G., *Surf. Sci.* **29**, 454 (1972).
35. Madix, R. J., and Telford, S. G., *Surf. Sci. Lett.* **328**, L576 (1995).
36. See, for instance, Zangwill, A., "Physics at Surfaces," Chap. 14. Cambridge Univ. Press, Cambridge, UK, 1988.
37. Holroyd, R. P., and Bowker, M., *Surf. Sci.* **377**, 786 (1997).
38. Hartmann, N., Esch, F., and Imbihl, R., *Surf. Sci.* **297**, 175 (1993).
39. Shekhar, R., and Barteau, M. A., *Catal. Lett.* **31**, 221 (1995).
40. Leibsle, F., and Bowker, M., *Catal. Lett.* **38**, 123 (1996).
41. See, for instance, Campbell, C. T., *Ann. Rev. Phys. Chem.* **41**, 819 (1990).