Direct synthesis of formate from methanol oxidation on the CuPd[85 : 15]{110}p(2 × 1) surface: induction of a new reaction pathway via a ligand effect

Mark A. Newton and Michael Bowker

Surface Science Research Centre and Leverhulme Centre for Innovative Catalysis,
Department of Chemistry, The University of Liverpool, Oxford Street, PO Box 147,
Liverpool L69 3BX, UK

Received 14 January 1993; accepted 8 June 1993

Thermal molecular beam studies of the oxidative dehydrogenation of methanol over the 1/4 ML and 1/2 ML oxygen predosed CuPd[85 : 15]{110}p(2 × 1) surfaces has been performed. Post reaction thermal desorption spectroscopy (TDS) clearly shows that during these experiments observable levels of formate are produced. This is in contrast to the results of similar experiments performed over oxidised Cu{110} surfaces which showed little formate production. It is hypothesised that the alloying in the surface region causes this new reaction pathway to appear as a consequence of a modification of the stability of one or more of the reactive intermediates produced in this reaction. It is proposed that these modifications of adsorbate stability are due to a ligand effect arising from the presence of Pd in the second layer of the selvedge.

Keywords: Methanol oxidation; oxidative dehydrogenation; formaldehyde production; alloy catalysis; Cu–Pd alloy; molecular beams; surface reactivity

The presence and significance of electronic or "ligand" effects in reactions occurring over alloy surfaces is of some considerable interest and debate in the field of catalysis. Unlike "ensemble" effects which are strictly a function of surface geometry and composition, the attribution of an observed effect in a reaction scheme solely to an electronic perturbation of the surface is very difficult. This is because, in most cases, the numbers and types of ensembles at the alloy surface are changed along with the electronic structure of that surface relative to the elemental case. Despite this some notable work (see for instance ref. [1]), principally on pseudomorphic metal overlayers, has produced some evidence for these effects for certain systems. One study on a bulk $Pd_3Cu\{111\}$ alloy [2] also presented some evidence for an electronic effect, though in this case the chemistry was dominated by ensemble effects. It is the purpose of this communication to report a significant perturbation of chemical reactivity, that is, the appearance of a new reaction pathway, due to surface alloying. It will be argued that this effect is solely the result of a ligand effect causing the destabilisation or stabilisation of individual reaction intermediates relative to Cu{110}.

The CuPd[85 : 15]{110}p(2 × 1) surface is highly unusual. A plan view of the surface is shown in fig. 1. The surface layer is devoid of Pd. The second layer, however, consists of an ordered array of CuPd. This structure has been derived from LEED [3], LEIS, and ARXPS experiments [4]. The dimensions of the surface in the surface plane have been determined to be only 1.3–1.6% greater than for Cu{110} ($\sim$ 0.05 Å in the {110} direction) [5,6]. Recent core level photoelectron diffraction experiments on this surface [7] show that interlayer expansions normal to the surface are caused by the high level of second layer Pd though these do not appear to be accompanied by any surface buckling. Further, the mode of reaction of this surface to adsorption of oxygen has also been shown to be identical to that seen for Cu{110}, that is with a similar sticking coefficient [8] and formation of a p(2 × 1) "missing row" surface [9]. Thus despite the alloy nature of this surface and the fact that the composition of the surface bilayer is a gross distortion of the bulk stoichiometry, both geometrically and compositionally the surface layer is very similar to Cu{110} in both the clean surface and oxygen covered cases. We have shown previously [4] that despite this conservation of surface geometry the electronic structure of this alloy is somewhat modified compared to that of Cu{110} due to a high degree of hybridisation and possibly charge transfer between the Cu and Pd states.

The oxidative dehydrogenation of methanol on Cu{110} has been studied by several groups [10–13] using various approaches. A bone of contention exists over whether it is possible to make formate directly from methanol on these oxidised surfaces; this is effectively the reverse of the proposed rate limiting hydrogenation of formate to give methanol in the methanol synthesis process, conducted over Cu based catalysts [14], and as such is of some interest. Wachs and Madix reported both the synthesis of formate [10], and later, a complete absence of this route [13] during TPD of methanol adsorbed on the 0.25 ML oxygen dosed Cu{110}. Gates et

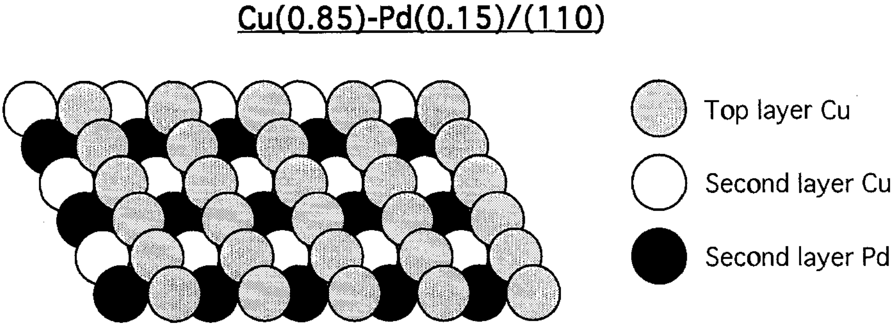

Fig. 1. The proposed structure of the CuPd[85 : 15]{110}p(2 × 1) surface, after Holmes et al. [3].

al. [11] have also reported formate synthesis from methanol on oxidised Cu{111}. Bowker and coworkers [12], however, using the same equipment as was used in this study, concluded from post reaction TPD and the absence of detectable CO_2 production during the beam experiments at higher temperatures, that there was no formate synthesis during the adsorption of methanol onto pre-oxidised Cu{110} surfaces and that all the methanol was reacted to form formaldehyde. Recent repetition of this work with a very high sensitivity TPD indicated a very low level of formate synthesis ($<2\%$ of the saturation coverage of formate on clean Cu{110} [15].

The current work was undertaken using the thermal molecular beam system described elsewhere [16], the beam flux being $\sim 2 \times 10^{13}$ mol cm^{-2}, the diameter of the beam being $\sim$ 2.8 mm. The system was also equipped with a mass spectrometer and LEED/Auger facilities. The sample cleaning procedures used to obtain the $p(2 \times 1)$ alloy surface have been documented elsewhere [4]. All gas dosing was performed using the beam source. CH_3OH and CD_3OD samples were purified using freeze–pump–thaw cycles until no impurities were found using the mass spectrometer. Preoxidation of the surface was performed using the beam source backed by 10 mbar oxygen, the level of preoxidation being determined by the length of time the sample was exposed to the beam. The details of the kinetics of oxygen uptake at this surface under these conditions, had been determined previously and will be published elsewhere [8]. After oxidation of the sample to a given level the oxygen was pumped away from behind the beam source capillary and replaced with 10 mbar of methanol vapour. The oxidised sample was then exposed to the methanol beam. Concurrently the uptake of methanol and the production of reaction products (water, hydrogen, formaldehyde, carbon dioxide, or their deuterated analogues) was monitored using the mass spectrometer. After cessation of the reaction at the surface (as evidenced by loss of product formation in the mass spectral trace), the sample was cooled and then subjected to a linear heating rate ($\sim$ 1.5 K s^{-1}) whilst the evolution of methanol, hydrogen, water, formaldehyde, and carbon dioxide was monitored. Data were collected over a range of sample temperatures for CH_3OH and CD_3OD dehydrogenation on both 0.25 ML and 0.5 ML predosed surfaces, 0.5 ML representing the saturation coverage under the dosing conditions used.

For the purpose of this communication we shall not consider the kinetics of the oxidative dehydrogenation process itself in any detail, but will simply present the post reaction TPD spectra. A typical spectrum, showing the five masses routinely followed, is shown in fig. 2 for an experiment performed at a sample temperature of 350 K. Fig. 3 shows D_2 TDS traces derived after dosing CD_3OD onto the alloy surface preoxidised with 0.25 ML oxygen, for a range of reaction temperatures.

Fig. 2 shows that no water was evolved during the TDS reaffirming the observation that the reaction has gone to completion and all the oxygen predosed to the surface has been used up (most of this as water which desorbs during the beaming of methanol, in a similar manner to Cu{110} [12]). The D_2 trace in fig. 2 betrays the

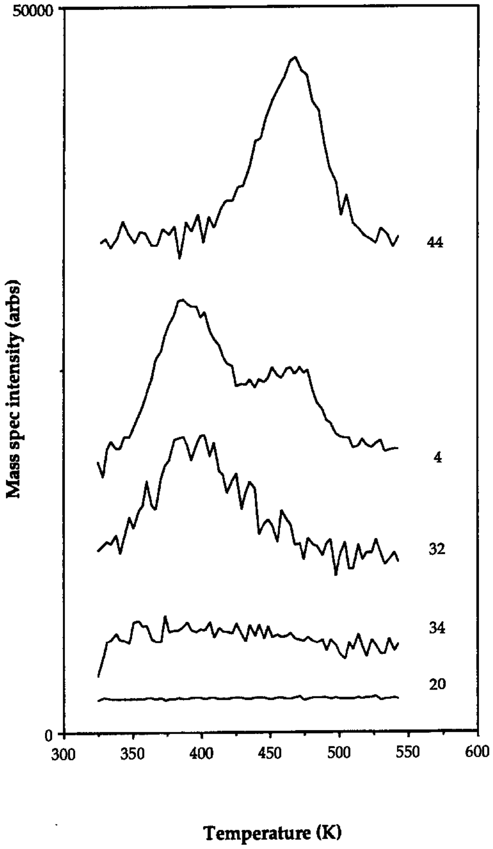

Fig. 2. Post reaction thermal desorption reaction spectrum derived from beaming CD_3OD onto the CuPd[85 : 15]{110}p(2 × 1) surface precovered with 0.25 ML adsorbed oxygen at 321 K. The experimental heating rate $\beta = 1.5$ K s^{-1}. The masses shown correspond to CO_2 (44), CD_2OD (34) (from intact CD_3OD), CD_2O (32), D_2O (20), and D_2 (4).

presence of two moieties that decompose and produce hydrogen. The lower temperature feature is associated with the concurrent evolution of a $m/e = 32$ fragment i.e. deuterated formaldehyde. This would indicate that this feature is derived from an adsorbed methoxy species which decomposes to yield hydrogen and formaldehyde coincidently [13]. The higher temperature state is seen to evolve concurrently with a $m/e = 44$ fragment, that is CO_2. From previous work [4] we know this coincident desorption pattern of H_2 and CO_2, at the temperatures in question, is indicative of the decomposition of a surface *formate* species. From fig. 3 it is evident that the amount of formate produced, as gauged by this feature and the concurrently obtained CO_2 TDS traces (not shown), appears also to be a sensitive function of surface temperature, though at higher temperatures CO_2 is also evolved during the beam experiment, and thus at these temperatures TDS alone does not accurately gauge the level of formate production.

Verification of the identity of the surface species giving rise to this higher tem-

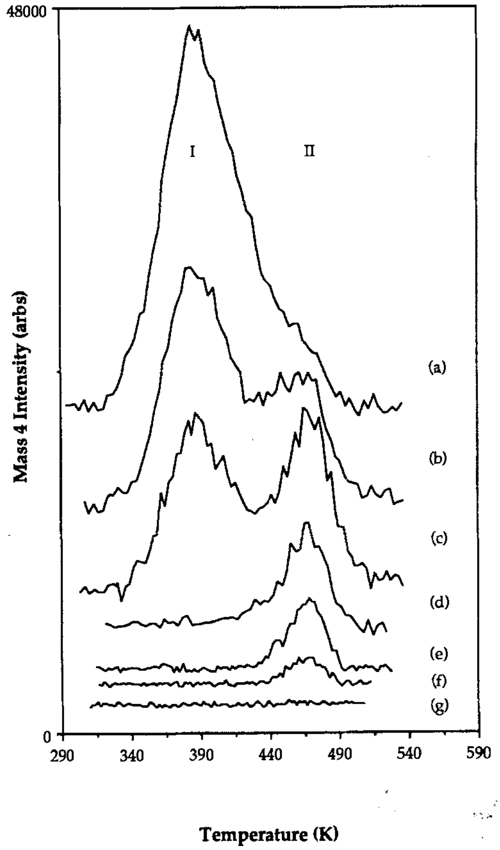

Fig. 3. D_2 (mass 4) evolution from post reaction TDS after exposure of the 0.25 ML oxidised surface to CD_3OD, showing the TDS D_2 yields due to methoxy dehydrogenation (I) and formate decomposition (II) with varying sample temperature. $\beta = 1.5$ K s^{-1}. The sample temperatures in each case are (a) 300 K, (b) 321 K, (c) 330 K, (d) 359 K, (e) 367 K, (f) 399 K, (g) 441 K.

perature state was obtained by dosing a clean surface with formic acid from the beam, until a saturation coverage was achieved, and then decomposing it on the alloy surface. This procedure not only allowed absolute identification of the TDS features as due to a formate species, but also allowed quantification of the amount of formate made during the beam experiments for each temperature of reaction. The results of this are shown in figs. 3 and 4, for runs at 0.25 ML initial coverage of oxygen. These results have been derived from integration of the CO_2 mass spectrometer trace for each thermal desorption experiment and, for higher temperature cases, from the CO_2 evolution curve derived during the beam experiments. The absolute coverages arise out of comparison of these integrals with those derived from the formic acid dosing experiments.

The level of formate produced during the beam experiments is a sensitive function of sample temperature. Significant amounts are only produced over a relatively narrow temperature range. The maximum amount of formate appears to be

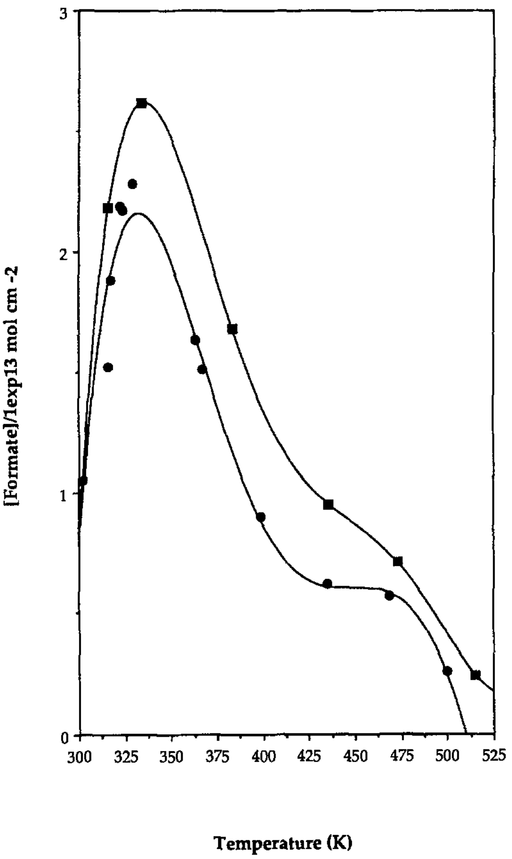

Fig. 4. The dependence of the degree formate synthesis during methanol beaming onto the 0.25 ML preoxidised alloy surface, as a function of temperature. The squares pertain to CH_3OH as a reactant, the filled circles to CD_3OD. The saturation coverage of formate on this surface [4] is ~ 2×10^{13} molecules cm^{-2}. The lines serve only to guide the eye.

around 0.1–0.14 of the saturation density (~ 2×10^{14} molecules cm^{-2} [4]) of formate at this surface. This corresponds to ~ 8–10% of the available oxygen in the 0.25 ML predosed case. Formate production is also noted in the 0.5 ML oxygen predosed case (not shown), though curiously, successive experiments performed at 0.25 and 0.5 ML show that the amount of formate produced in each case, at a given temperature, is the same despite the fact that in the latter case there is twice as much oxygen present at the surface.

The reaction pathway leading to formate is therefore relatively minor in terms of the overall conversion of methanol. However it is significant, as this product synthesis route *does not occur to any appreciable degree* under the same conditions for Cu{110} [12,15].

The question arises as to why this reaction pathway has become available to reacting molecules on the alloy surface where it is much less accessible on Cu{110}? Detailed analysis of the kinetics of the overall dehydrogenation of methanol will be given elsewhere [8], however, a noteworthy point in the current context is that at lower reaction temperatures (<400 K) the formaldehyde production is faster on the alloy surface than is observed for Cu{110} [12]. Above this temperature the rates of formaldehyde production, on each surface appear to become comparable. The overall mechanism of reaction, however, appears the same as on Cu{110} in terms of formaldehyde production, that is,

$$CH_3OH_{(g)} + O_{(a)} \rightarrow CH_3O_{(a)} + OH_{(a)} \tag{1}$$

$$CH_3OH_{(g)} + OH_{(a)} \rightarrow CH_3O_{(a)} + H_2O_{(g)} \tag{2}$$

$$CH_3O_{(a)} \rightarrow CH_2O_{(a)} + H_{(a)} \tag{3}$$

$$2H_{(a)} \rightarrow H_{2(g)} \tag{4}$$

$$2H_{(a)} + O_{(a)} \rightarrow H_2O_{(g)} . \tag{5}$$

At low temperatures step (3) determines the rate of production of formaldehyde. Steps (4) and (5) compete though the dominant reaction is the formation of $H_{2(g)}$ through step (4) as most of the surface oxygen has already left the surface as a result of step (2). The formation of formate within this scheme is most likely due to the following:

$$CH_2O_{(a)} + O_{(a)} \rightarrow CH_2O_{2(a)} \tag{6}$$

$$CH_2O_{2(a)} \rightarrow CHO_{2(a)} + H_{(a)} . \tag{7}$$

Evidence for the production of the biformate moiety ($CH_2O_{2(a)}$) in a similar reaction scheme over Ag{110} was given previously [17]. On Cu{110} the presence of this intermediate cannot be determined from TDS, due to the stability of the $H_{(a)}$ produced in step (7) at the temperature of biformate decomposition, but is inferred from the reaction on Ag{110}.

Thus whether formate synthesis will occur under these conditions depends heavily on the availability of adsorbed formaldehyde and the presence of adsorbed oxygen. It is known that step (6) is facile on Cu{110} [18] so it is unlikely that it is the kinetic parameters describing the nucleophilic attack of oxygen upon the formaldehyde species that determine formate synthesis. It appears likely that the reason for the appearance of a formate synthesis pathway on the alloy surface is related to the stabilities of the adsorbed methoxy and/or formaldehyde species on the alloy surface relative to Cu{110}. We have evidence from a previous study [4] concerning the decomposition of formate at this alloy surface that these sorts of effect can occur. In that case we found that the stability of the formate on the p(2 × 1) alloy surface was decreased, though the mechanism of the decomposition process was conserved relative to that seen on Cu{110}.

We can gain an estimate of the decomposition energy of $CH_3O_{(a)}$ from the TDS spectra. Using the Redhead approximation for first order desorption [19] that is,

$$E_d/RT_{max} = \ln(\nu_d T_{max}/\beta) - 3.46$$

with $\nu_d = 10^{13}$ s^{-1} and T_{max} (from the TDS spectra) of 385 K, and β (the experimental heating rate) $= 1.5$ K s^{-1}, then E_d for the dehydrogenation of $CD_3O_{(a)} \approx 102$ kJ mol^{-1}. This compares with a similarly derived value for $CH_3O_{(a)}$ dehydrogenation of ~ 98 kJ mol^{-1} (from [13] with $T_{max} \approx 380$ K and $\beta = 4$ K s^{-1}). Modelling of the methanol dehydrogenation process on Cu{110} by Bowker and coworkers [12] suggested the presence of an unusually large isotope effect in the methoxy dehydrogenation on Cu{110} ($\sim$ 10 kJ mol^{-1}). An isotope effect is evident both from the overall rates of formaldehyde production in the beam experiments [8], and the fact that post reaction TDS from reactions using CH_3OH (not shown) shows that no adsorbed $CH_3O_{(a)}$ is left at the surface after reaction even at the lowest run temperatures for CH_3OH of 314 K. This implies a considerably greater instability of $CH_3O_{(a)}$ on this surface than is seen for its deuterated counterpart. If this effect, in this case, is of the magnitude of that seen for Cu{110} [12], then one could infer that the methoxy species on the alloy surface may be less stable than on Cu{110} by $\sim$ 5 kJ mol^{-1}. The rate of production of adsorbed formaldehyde at 350 K, for instance, would therefore be of the order of six times greater on the alloy surface. This small difference in stabilities of a key reaction intermediate could well allow appreciable amounts of $H_2CO_{(a)}$ to be formed in the presence of $O_{(a)}$ at lower temperatures and thus allow formate synthesis.

These data suggest that a destabilisation of the methoxy species is occurring relative to Cu{110}. The observed temperature dependence of the amount of formate formed during the reactions, thus becomes qualitatively explainable as does the absence of this reaction pathway on Cu{110}.

At low temperatures the rate of dehydrogenation of the adsorbed methoxy becomes slow and the methoxy species is stable on the alloy surface. The rate of adsorption of methanol within this temperature range is relatively independent of temperature and the water formation reaction is fast. Thus as the surface temperature is lowered the amount of $H_2CO_{(a)}$ being produced from methoxy decomposition in the presence of $O_{(a)}$ becomes very small. Thus even if the surface lifetime of a $H_2CO_{(a)}$ molecule at the alloy surface is increased the rate of production of this moiety becomes so slow relative to oxygen removal as water that formate synthesis becomes increasingly improbable as the sample temperature is decreased.

At higher temperatures the production of $H_2CO_{(a)}$ is much faster due to the increasing instability of the methoxy species toward dehydrogenation. However, the surface lifetime of formaldehyde will be diminished and becomes the determining factor in formate synthesis. Thus again the probability of a surface formaldehyde species finding an adsorbed oxygen atom diminishes and the probability of formate synthesis is reduced. Hence the temperature window in which formate is evolved on the alloy surface represents a special set of circumstances where the rate of dehydrogenation of the adsorbed methoxy species is fast enough to produce appreciable quantities of $H_2CO_{(a)}$, with a long enough surface lifetime, to allow it to react with $O_{(a)}$, whilst there is still some $O_{(a)}$ still present at the surface.

Currently further work is underway to develop a kinetic model which will describe and account for the observed differences both in the rates of methanol oxidation over the alloy and the Cu{110} surface and the presence or lack of a formate synthesis pathway for each surface. Further experimental work is also being undertaken in an attempt to verify the hypothesis that the stabilities of $CH_3O_{(a)}$ and/or $H_2CO_{(a)}$ are modified on the alloy surface relative to Cu{110} in the manner outlined above. It must be emphasised, however, that the effects observed could be caused by very small perturbations in the stability of the species involved and may not be definitively resolvable in a thermal desorption experiment.

That these differences in chemistry exist, however, is not in doubt. The alloy surface is effectively showing a greater tendency for total combustion of methanol, formate decomposition leading directly to CO_2. From the idea of "microscopic reversibility" these observations would imply that an adsorbed methoxy species will be more easily formed from hydrogenation of a formate moiety on the CuPd[85 : 15]{110}p(2 × 1) surface than on Cu{110}. By the same principle we already know that formate formation from CO_2 and H_2 should be easier on this alloy surface than on Cu{110} (from the results of TDS experiments on formate decomposition [4]). Overall the implication is that methanol synthesis from $CO_{2(g)}$ and $H_{2(g)}$ on this alloy surface might be more facile than on Cu{110}.

What is the source of the modifications of adsorbate stability that cause this new reaction pathway to exist? From what we know about the clean surface structure [4,7] and the structure of the reconstructed oxygen covered surface [9], attribution of these effects to surface Pd or differences in the ensembles available at the alloy or Cu{110} surfaces is ruled out. We do know that the electronic structure of this alloy surface is significantly different to that seen for Cu{110} [4], and it seems most likely it is in these differences that the source of the modified chemistry lies. Thus, it would seem that the new chemistry observed at the CuPd[85 : 15]-{110}p(2 × 1) surface is solely the result of a ligand effect.

Acknowledgement

The authors would like to thank SERC and ICI Katalco for the provision of a studentship to MN.

References

[1] J.A. Rodriguez and D.W. Goodman, J. Phys. Chem 95 (1991) 4196.
[2] A. Noordermeer, G.A. Kok and B.E. Nieuwenhuys, Surf. Sci. 172 (1986) 349.

[3] D.J. Holmes, D.A. King and C.J. Barnes, Surf. Sci. 227 (1990) 179.
[4] M.A. Newton, S.M. Francis and M. Bowker, Surf. Sci. 259 (1991) 45.
[5] R.S. Rao, A. Bansil, H. Aasonen and M. Pessa, Phys. Rev. B 35 (1987) 1713.
[6] M. Lindroos, C.J. Barnes, M. Bowker and D.A. King, in: *Proc. ICSOS III, The Structure of Surfaces III*, Springer Series in Surface Sciences 24, eds. S.Y. Tong, M.A. Van Hove, K. Takayanagi and X.D. Xie (Springer, Berlin, 1990) p. 287.
[7] M.A. Newton, S.M. Francis and M. Bowker, Phys. Rev. Lett., submitted.
[8] M.A. Newton and M.A. Bowker, to be published.
[9] M.A. Newton, S.M. Francis and M. Bowker, Phys. Rev. B 45 (1992) 945;
M.A. Newton, S.M. Francis and M. Bowker, Surf. Sci. 269/70 (1992) 41.
[10] I. Wachs and R.J. Madix, J. Catal. 53 (1978) 208.
[11] S.M. Gates, J.N. Russel Jr. and J.T. Yates Jr., Surf. Sci. 159 (1985) 233.
[12] C.J. Barnes, P.D.A. Pudney, Q. Guo and M. Bowker, J. Chem. Soc. Faraday. Trans. 86 (1990) 2693.
[13] M. Bowker and R.J. Madix, Surf. Sci. 102 (1981) 542.
[14] G.C. Chinchen, P.J. Denny, M.S. Spencer and K.C. Waugh, Appl. Catal. 36 (1988) 1.
[15] S.M. Francis, S. Haq, N. Xiang and M. Bowker, in preparation.
[16] M. Bowker, P.D.A. Pudney and C.J. Barnes, J. Vac. Sci. Technol. A 8 (1990) 816.
[17] M.A. Barteau, M. Bowker and R.J. Madix, Surf. Sci. 94 (1980) 303.
[18] M. Bowker and R.J. Madix, Surf. Sci. 95 (1980) 195.
[19] P.A. Redhead, Vacuum 12 (1962) 203.