Oxidation of methanol at copper surfaces

A.F. Carley, A.W. Owens, M.K. Rajumon, M.W. Roberts

Department of Chemistry, University of Wales, Cardiff, PO Box 912, Cardiff CF1 3TB, UK

and

S.D. Jackson

ICI Katalco, R, T & E Group, PO Box 1, Billingham, Cleveland, TS23 1LB, UK

Received 21 September 1995; accepted 7 November 1995

The role of preadsorbed oxygen present at Cu(111), Cu(110) and polycrystalline surfaces in the oxidation of methanol has been investigated by X-ray and electron energy loss spectroscopies. In addition to the well established formation of methoxy species and its subsequent decomposition and desorption as formaldehyde, a second reaction pathway to surface formate is present. The latter is temperature dependent being undetectable at 260 K at a polycrystalline surface but occurs at a significant rate at 295 K and above. The limitations of experimental data for methanol oxidation by temperature programmed desorption and molecular beam techniques are discussed.

Keywords: methanol; oxidation; copper; electron spectroscopy

1. Introduction

Mechanistic studies of the oxidation of methanol at single crystal surfaces of copper have, in the main, relied upon data from molecular beam (MB) [1] and temperature programmed desorption (TPD) [2–4] experiments. More recently, scanning tunneling microscopy has also been used [5–7]. Both MB and TPD rely on the analysis of the gaseous products arising from the oxidation reaction which are mainly formaldehyde and hydrogen. The TPD experiment also suffers from the inherent disadvantage of the temperature ramping having a possible influence on the chemistry occurring at a particular temperature. However, neither experimental method provides data on how the reaction proceeds *at the surface* in real time at a given temperature. Whether any changes occur at the surface – for example, is formate generated subsequent to methoxy formation – is explored by heating to ~ 450 K and monitoring whether or not CO_2 is desorbed, the latter being taken as diagnostic of surface formate. The results with Cu(110)–O are conflicting: Barnes et al. [1] concluded that "the formate species is not formed in any significant quantities" for a range of oxygen precoverages, whereas Francis et al. [6] reported "small amounts of CO_2 at 440 K" which implies the presence of surface formate. It is worth noting in the context of the present work that mass-spectroscopic studies of methanol decomposition at nickel and oxidation at gold surfaces reported by one of the present authors [8] in 1970 indicated, in addition to formaldehyde, water, and hydrogen, the formation of hydrocarbons (methyl formate and methane) arising from carbon–oxygen bond cleavage at 295 K.

The present work is the first detailed quantitative analysis of X-ray photoelectron spectra observed in real time, under constant temperature conditions, of the interaction of methanol with pre-oxidised Cu(110), Cu(111) and polycrystalline copper surfaces. It addresses the question of the stoichiometry of the oxygen induced reaction, i.e. how many methoxy groups form per surface oxygen preadsorbed and, also, whether the core-level spectra provide any evidence for a surface reaction subsequent to methoxy formation. The results are particularly significant in the interpretation of real-time scanning tunneling microscopy studies.

In the analogous activation of ammonia by oxygen at copper surfaces, distinction has been made between preadsorbed and coadsorbed oxygen with experimental evidence being supported by van Santen's [9] density functional calculations for low energy pathways to imide/amide species involving surface oxygen transients. In the case of preadsorbed oxygen, the active oxygens in H-abstraction from ammonia are suggested to be those positioned at the end of Cu–O–Cu–O chains – this conclusion was based on a Monte Carlo simulation of the oxide overlayer at Cu(110) compared with the experimentally observed activity in NH_x formation as a function of oxygen coverage [10]. The conclusion, which we believe is of general significance [11], is that high chemical reactivity associated with surface oxygen at the copper surface can be maintained provided oxygen clusters (islands) are not allowed to develop and that it is the charge on the oxygen that is the crucial factor.

Recent STM investigations of the Cu(110)–O–methanol system also relate oxygen activity with those adatoms situated at the end of these chains [5–7].

2. Experimental

A modified VG Scientific ESCA 3 photoelectron spectrometer, a hybrid PES (VG Scientific)–VEELS (Vacuum Science Workshop) spectrometer and a custom designed spectrometer (V.G. Scientific) were used in this investigation. The Cu(110) and Cu(111) crystals (Metal Crystals Ltd) were mechanically polished using 1 μ diamond paste. In situ cleaning consisted of cycles of argon ion bombardment and vacuum annealing (673 K). The polycrystalline copper was spec pure and obtained from Metals Ltd.

The methanol (99.9%) (Matheson Gas Products) was purified on a UHV gas handling and admission system using several freeze–pump–thaw cycles. The oxygen (P.J. Mason, 99.99%) was introduced to the spectrometer via a liquid nitrogen cooled cold finger, in order to remove any trace condensible impurities.

Spectra were acquired using both an Apple II-based data system developed in-house, and an IBM-compatible microcomputer (OPUS V) running commercial data acquisition software (SPECTRA). Analysis was performed using software developed in this laboratory [12], and adsorbate surface concentrations calculated from integrated peak intensities [12,13]. XPS core-level binding energies were calibrated against the clean Cu($2p_{3/2}$) photoemission peak at 932.7 eV.

3. Results and discussion

3.1. Methanol adsorption on clean copper surfaces

We observed no significant reaction between methanol and both clean Cu(110) and polycrystalline copper surfaces at 295 K, even after exposures of several hundred langmuirs [#1].

3.2. Methanol adsorption on pre-oxidised Cu(110) and Cu(111) surfaces

Fig. 1 shows the VEEL spectrum observed after exposing a pre-oxidised Cu(110) surface to methanol at 295 K. The pre-oxidised spectrum shows a single strong loss peak at 400 cm^{-1} corresponding to ν(Cu–O). A weak feature observed at ca. 1000 cm^{-1} after only 5 L exposure to methanol increases greatly in intensity with further exposure. After $\sim$ 20 L exposure it is centred at 1050 cm^{-1} and accompanied by loss peaks at 1400 cm^{-1} and ca. 2900 cm^{-1}. These features arise from the vibrational modes $\nu(H_3C–O)$, $\delta(CH_3)$ and ν(C–H) of adsorbed methoxy species [14], CH_3O(a); the assignments are indicated in fig. 1. The VEEL spectra, however, do not provide quantitative information regarding the surface concentrations of the preadsorbed oxygen and methoxy species. For this we turn to the XPS data.

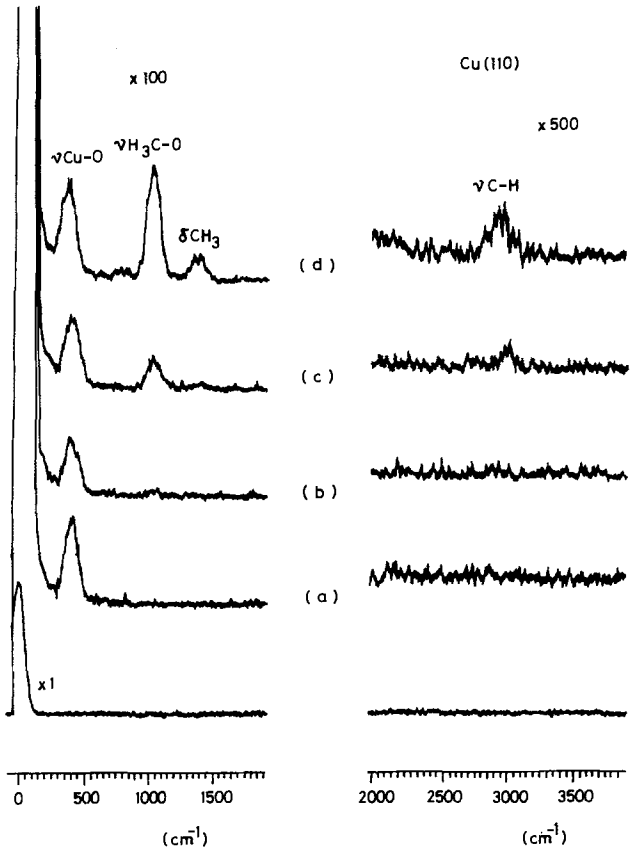

Fig. 1. VEEL spectra for the adsorption of methanol on a Cu(110)–O surface at 298 K: (a) clean surface exposed to dioxygen (1 L) at 298 K, followed by exposure to methanol: (b) 5 L, (c) 10 L, (d) 20 L.

O(1s) spectra for the replacement of chemisorbed oxygen by methoxy species are shown in fig. 2. Chemisorbed oxygen is characterised by a peak at a binding energy 529.8 eV. On exposure to methanol a new feature develops at 530.9 eV at the expense of the 529.8 eV peak, until after an exposure of 18 L it dominates the O(1s) region. Concomitant with this, a C(1s) peak at 285.5 eV binding energy appears and grows in intensity with methanol exposure, as the chemisorbed oxygen atoms are replaced by methoxy species. *The most important observation, however, is that the integrated intensity of the O(1s) spectrum remains constant through the replacement reaction.* This is clear from a visual inspection of fig. 2, and is confirmed by the calculated surface concentrations – the initial oxygen adatom concentration, and the final concentration of oxygen containing species (after 18 L methanol exposure) is 2.95×10^{14} cm^{-2}. A curve-fit of the O(1s) spectral region shows that 88% of the original chemisorbed oxygen $O^{\delta-}$(a) has been replaced by CH_3O(a) i.e. a $CH_3O : O^{\delta-}$

[#1] 1 L (langmuir) = 10^{-6} Torr s.

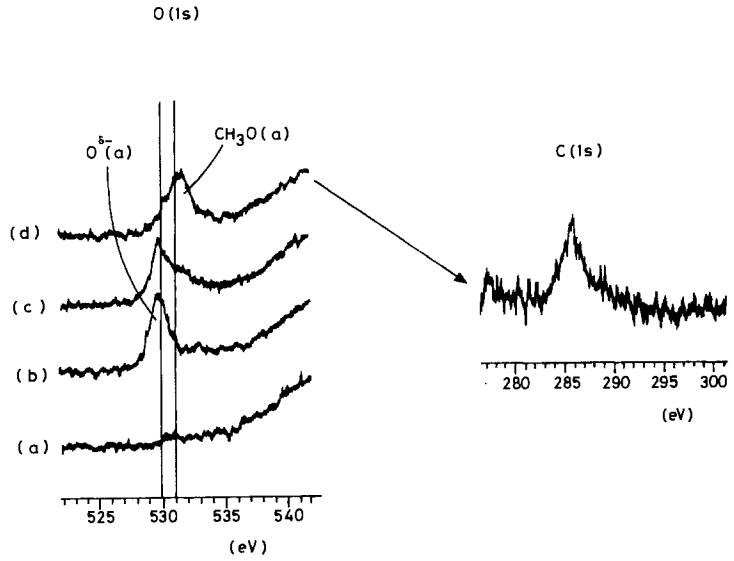

Fig. 2. O(1s) spectra for the chemisorptive replacement of adsorbed oxygen by methoxy species on Cu(110) at 298 K: (a) clean surface, (b) exposed to dioxygen (1 L), (c) exposed to 6 L methanol, (d) exposed to a total of 18 L methanol. The C(1s) spectrum corresponding to (d) is also shown.

ratio close to unity. The results for a number of other similar experiments with different initial coverages of $O^{\delta-}(a)$ also indicate a replacement ratio close to unity. The VEEL spectra show no evidence for the presence of OH(a).

The reaction stoichiometry observed with the Cu(111)–O surface (fig. 3) contrasts sharply with that for Cu(110)–O. It is clear from the XPS data (fig. 3) that the O(1s) intensity increases significantly as the replacement of chemisorbed oxygen by methoxy species proceeds. Indeed, after an exposure of 20 L of methanol, the total "oxygen" concentration has increased from 1.5×10^{14} cm^{-2} to 2.9×10^{14} cm^{-2}, the ratio CH_3O (adsorbed) : $O^{\delta-}$ (removed) being close to 2 : 1. In order to understand the difference between the reactivities of the Cu(111) and Cu(110) surfaces, we will first consider the generally accepted reaction mechanism for methoxy formation and whether more recent studies by different experimental approaches support it.

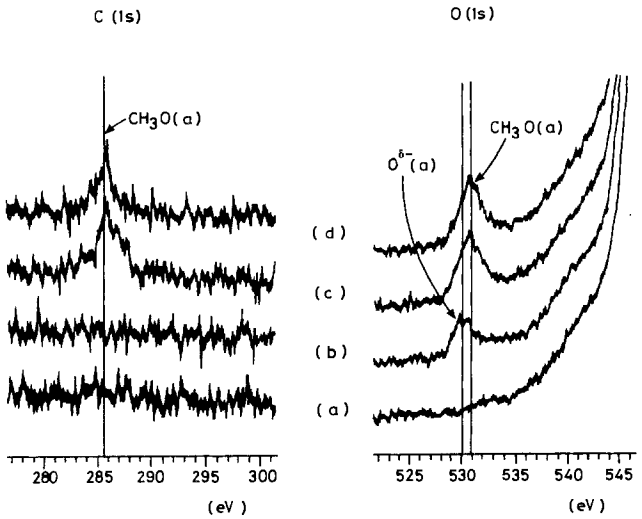

Fig. 3. C(1s) and O(1s) spectra for methoxy formation at a pre-oxidised Cu(111) surface at 298 K: (a) clean surface, (b) exposed to 75 L dioxygen, (c) exposed to 10 L methanol, (d) exposed to 20 L methanol.

3.3. Reaction mechanism for methanol oxidation

The reaction steps involved in the formation of, initially, methoxy species, and subsequently formaldehyde, at copper surfaces have until recently been derived indirectly from TPD and molecular beam experiments, primarily with Cu(110) surfaces. Studies by Madix and Bowker [1,2,4] led to the following reaction scheme being proposed at 300 K for the Cu(110) surface:

$$CH_3OH(g) \rightarrow CH_3OH(a) \quad (1)$$

$$O^{\delta-}(a) + CH_3OH(a) \rightarrow CH_3O(a) + OH(a) \quad (2)$$

$$OH(a) + CH_3OH(a) \rightarrow CH_3O(a) + H_2O(a) \quad (3)$$

$$H_2O(a) \rightarrow H_2O(g) \quad (4)$$

These result in the overall reaction (5)

$$O^{\delta-}(a) + 2CH_3OH(g) \rightarrow 2CH_3O(a) + H_2O(g) \quad (5)$$

for which the expected CH_3O : $O^{\delta-}$ ratio would be 2 : 1. This is clearly not in agreement with our XPS data for Cu(110), which provide a direct spectroscopic analysis of the surface and unambiguous quantification of the concentrations of adsorbed species. In the present work the CH_3O : $O^{\delta-}$ ratio is simply equal to the ratio of two O(1s) peak areas, and requires no other assumptions or parameters. On the other hand analogous data for Cu(111) agree with the conclusions of the above reaction scheme (eq. (5)).

Since the formation and desorption of water during

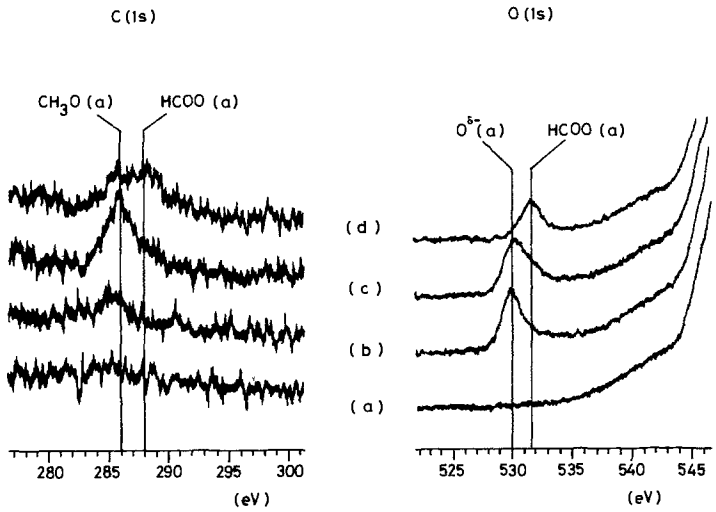

Fig. 4. Surface formate production from a mixed $CH_3O/O^{\delta-}$ adlayer on Cu(110) C(1s) and O(1s) spectra: (a) clean surface, (b) exposed to 1 L O_2, (c) exposed to 20 L methanol to generate methoxy species, (d) left overnight in vacuo.

methanol oxidation, established by TPD, suggests that reaction steps (1)–(4) are likely to be correct then it follows that at Cu(110)–O surfaces, approximately half of the methoxy species formed disappear relatively rapidly from the surface. On the other hand with Cu(111) all the surface methoxy species formed in the reaction are stable at 300 K, and the ratio $CH_3O : O^{\delta-}$ is 2 : 1 (eq. (5)).

The question that has to be addressed is what other possible pathway is available to CH_3O(a) other than desorption as formaldehyde.

3.4. Oxidation of methoxy species to formate

If a mixed CH_3O(a)/O(a) adlayer present on a Cu(110) surface is left overnight in UHV, significant changes were observed in both the XP and VEEL spectra (figs. 4, 5). In the C(1s) spectral region, the feature associated with the methoxy species decreases markedly in intensity and a new peak at 288 eV binding energy develops. The O(1s) component attributed to $O^{\delta-}$(a) disappears completely, but with intensity now present at a binding energy of 531.6 eV i.e. significantly higher than that characteristic of adsorbed methoxy. These observations are consistent with the presence of adsorbed formate species [14–17], and this is corroborated by the VEELS data (fig. 5). The loss features due to methoxy are reduced in intensity and new features are observed characteristic of a bidentate formate species: O–C–O bend (780 cm^{-1}), symmetric O–C–O stretch (1350 cm^{-1}) and C–H stretch (2800 cm^{-1}). There is no evidence for an asymmetric stretch loss, in keeping with the RAIRS study of formic acid on Cu(110) reported by Hayden et al. [18]. This was interpreted in terms of an adsorption site with C_{3v} or $C_s(1)$ symmetry. NEXAFS [19] and ARUPS [20] measurements for formate adsorbed on Cu(110) are consistent with a symmetric upright orientation for HCOO(a).

With Cu(111) no formate species are generated but we observe a decrease in intensity of those spectral features characteristic of adsorbed methoxy species (fig. 6).

3.5. Methanol adsorption on pre-oxidised polycrystalline copper surfaces

The single crystal studies were extended by investigating similar reactions with Cu(pc) (polycrystalline cop-

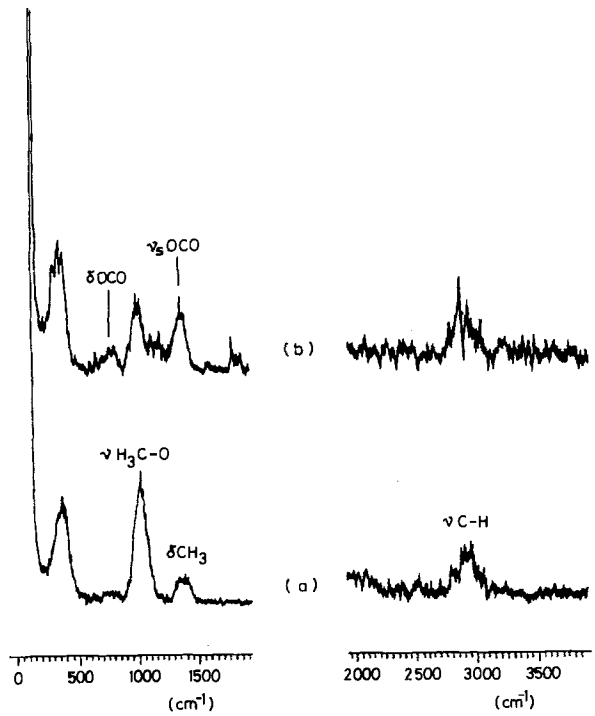

Fig. 5. VEEL spectra corresponding to the experiment of fig. 4: (a) mixed $CH_3O/O^{\delta-}$ adlayer on Cu(110), (b) left overnight in vacuo.

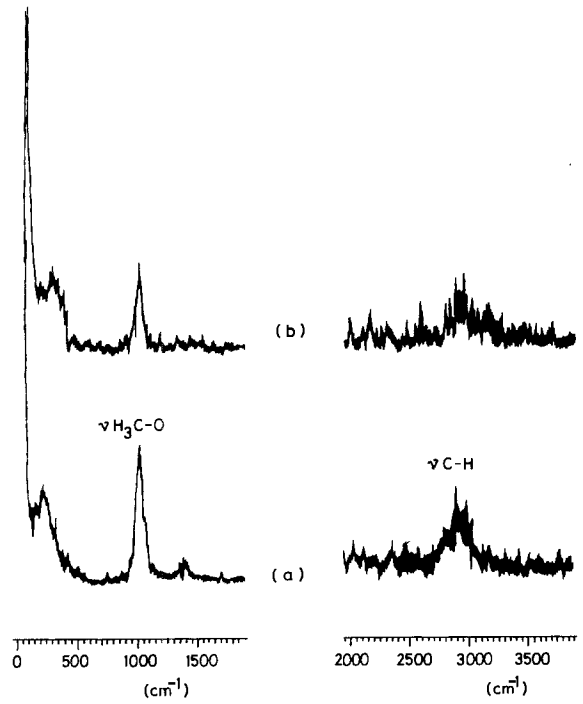

Fig. 6. Evidence from VEEL spectra that methoxy species are not oxidised to formate on Cu(111): (a) mixed $CH_3O/O^{\delta-}$ adlayer, (b) left overnight in vacuo.

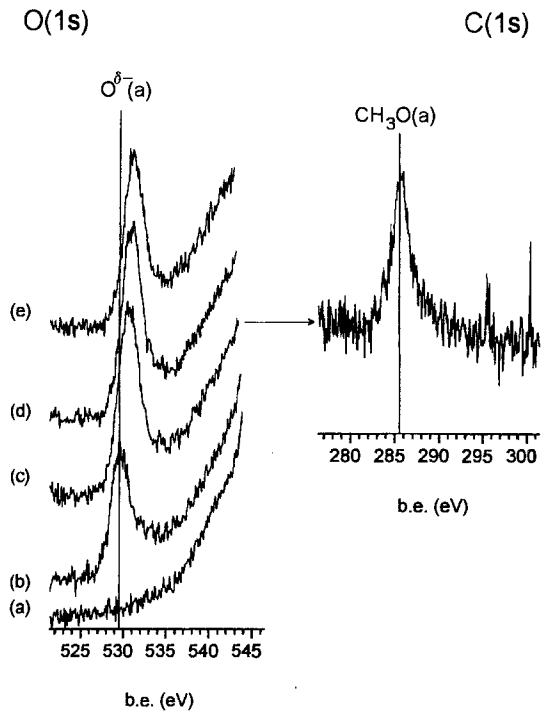

Fig. 7. O(1s) spectra for the step-wise adsorption of methanol at a pre-oxidised Cu(pc) surface at 295 K: (a) clean surface, (b) after exposure to dioxygen (7 L) at 295 K – $\sigma_0 = 0.36 \times 10^{15}$ cm^{-2}; subsequent accumulative exposures to methanol at 295 K were (c) 10 L, (d) 40 L, (e) 100 L; the surface concentration of methoxy species at this stage is 0.47×10^{15} cm^{-2}. The C(1s) spectrum for adsorbed methoxy, corresponding to (c), is also shown.

per) surfaces, with the aim of exploring whether the concepts that emerged from the data obtained with Cu(110) and Cu(111) were of more general significance.

In fig. 7 are shown the O(1s) and C(1s) spectra for a pre-oxidised polycrystalline copper surface ($\sigma_0 = 0.36 \times 10^{15}$ cm^{-2}) exposed to sequential doses of methanol at 295 K. Apparently similar behaviour is observed as that with the Cu(110) surface, a total of 100 L of methanol resulting in complete conversion of the preadsorbed oxygen $O^{\delta-}(a)$ to methoxy species, with a final methoxy concentration close to that of the original chemisorbed oxygen. These data, however, conceal surface chemistry which is more subtle than is apparent in fig. 7. This is clear from the spectra observed when a pre-oxidised polycrystalline copper surface ($\sigma_0 = 0.23 \times 10^{15}$ cm^{-2}) is exposed to a *single* dose of methanol sufficient to result in complete consumption of the preadsorbed oxygen $O^{\delta-}(a)$ (fig. 8). In this case the reaction stoichiometry [$CH_3O(a)$ formed] : [$O^{\delta-}(a)$ reacted] is 2 : 1, in contrast with the 1 : 1 stoichiometry observed for sequential dosing of Cu(pc) (fig. 7) and Cu(110) (fig. 2). The C : O atom ratio deduced from the C(1s) and O(1s) peak intensities is 1.2 : 1, consistent with the assignment to methoxy species. However, the intensities of both the O(1s) and particularly the C(1s) peaks decrease significantly with time in vacuo, and after 100 min the concentration of surface species estimated from the O(1s) intensity is only 0.34×10^{15} cm^{-2}. The small but reproducible shift observed in the binding energy of the O(1s) feature at this stage, compared with that characteristic of the initial methoxy species, is due to the formation of surface formate, which occurs concomitant with the loss of methoxy species from the surface. The O(1s) peak is therefore composite, consisting of contributions from both methoxy and formate species. We will return to this point.

The stability of the methoxy species at the copper surface is strongly dependent on sample temperature. At 260 K (fig. 9) the methoxy species is again produced in a 2 : 1 ratio compared with the initial concentration of chemisorbed oxygen, but the O(1s) peak intensity decreases by only ca. 10% even after 3 h in vacuo. Furthermore, there is no shift in the O(1s) binding energy during this period, indicating that formate production is negligible.

The generation of formate from chemisorbed methoxy may, however, be accelerated by heating the adlayer to 350 K (fig. 10). The species produced is characterised by O(1s) and C(1s) binding energies of 531.3 and 287.3 respectively, and an atomic ratio O : C of 2 : 1. The final concentration of surface formate is essentially identical with the initial concentration of chemisorbed oxygen before exposure to methanol. In other words, about 50% of the original methoxy species have reacted to produce formate, the rest decomposing and disappearing from the surface.

In order to confirm the assignment of the O(1s) and C(1s) peaks to formate species, we exposed a clean

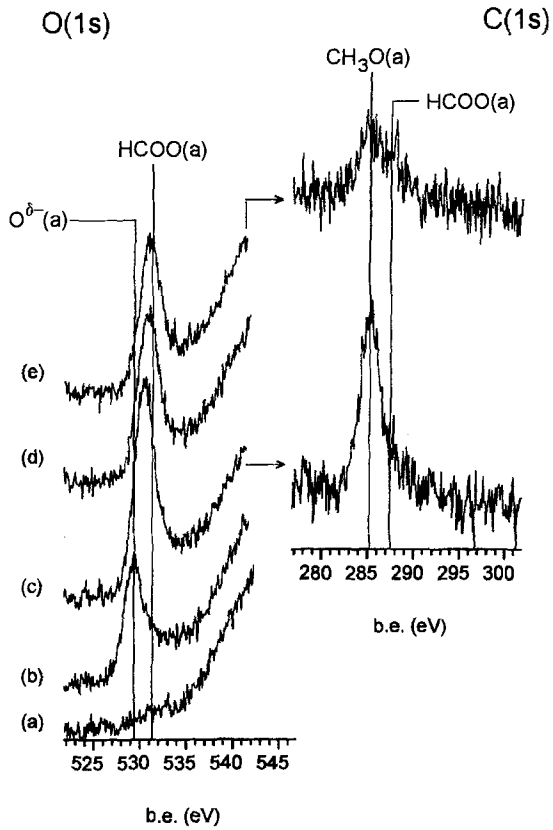

Fig. 8. O(1s) spectra observed when a pre-oxidised Cu(pc) surface is exposed at 295 K to a single methanol dose sufficient to react with all the chemisorbed oxygen atoms $O^{\delta-}(a)$: (a) clean surface, (b) pre-oxidised surface – $\sigma_o = 0.23 \times 10^{15}$ cm^{-2}, (c) after exposure to methanol (20 L). The O(1s) spectra were then recorded after leaving the surface in vacuo at 295 K for (d) 100 min, (e) 180 min; at this stage $\sigma_o = 0.31 \times 10^{15}$ cm^{-2}. C(1s) spectra corresponding to (c) and (e) are also shown.

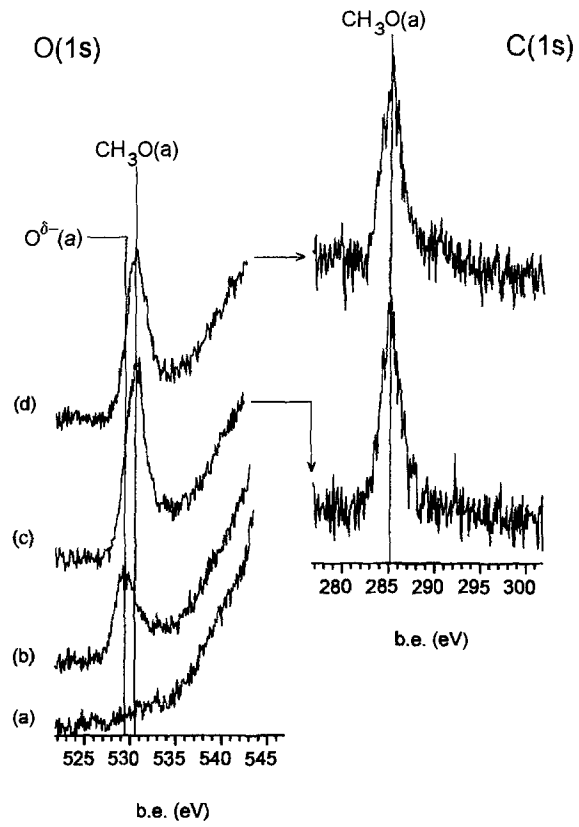

Fig. 9. O(1s) and C(1s) spectra showing the effect of temperature on methoxy decomposition at Cu(pc) surface: (a) clean surface, (b) pre-oxidised at 295 K – $\sigma_o = 0.19 \times 10^{15}$ cm^{-2}, (c) after reaction with methanol at 260 K to give methoxy species – $\sigma_o = 0.43 \times 10^{15}$ cm^{-2}, (d) after 180 min in vacuo at 260 K; at this stage $\sigma_o = 0.37 \times 10^{15}$ cm^{-2}.

Cu(pc) surface to formic acid at room temperature (fig. 11); the resulting O(1s) and C(1s) peaks had binding energies in excellent agreement with those observed in fig. 10. The formate species are stable at 400 K but decomposed readily at 473 K to products which desorb from the surface (fig. 11). Thus, at 350 K our observations (fig. 12) are not affected by any thermally induced changes in the formate population.

The kinetics of methoxy decomposition and formate production were studied by generating surface methoxy species as already described and monitoring the O(1s) spectrum at regular intervals at 295 K in vacuo (fig. 12). Since we have experimental values for the O(1s) binding energies and FWHM for pure methoxy and formate species (figs. 9 and 11) we can perform a least-squares curve-fit analysis of these composite spectra with the peak intensities as the only variables (fig. 12). The concentrations derived for the two species are plotted (fig. 12) as a function of time in vacuo. After ca. 3 h the concentration of formate species has saturated and the rate of decrease in methoxy species has slowed down. However, on heating to 350 K the formate concentration remains unchanged whereas the methoxy concentration has decreased below detection limits.

3.6. *Mechanistic implications of the observations with polycrystalline copper*

There is clear and unambiguous evidence from the XP spectra that two reaction pathways are possible subsequent to methoxy formation on polycrystalline copper:

(1) Decomposition and desorption as formaldehyde [1, and references therein]

$$CH_3O(a) \rightarrow H_2CO(g) + H(a) \qquad (6)$$

(2) The formation of surface formate. This occurs at a negligible rate at 260 K, is slow at 295 K and proceeds rapidly at 350 K. Since formate species are formed *after* all of the initial chemisorbed oxygen has been consumed, the reaction cannot be a simple oxidation of methoxy by oxygen adatoms.

One possibility is that it is formed via the elimination of methane from two adjacent methoxy species

$$2CH_3O(a) \rightarrow HCOO(a) + CH_4(g) + \tfrac{1}{2}H_2(g) \qquad (7)$$

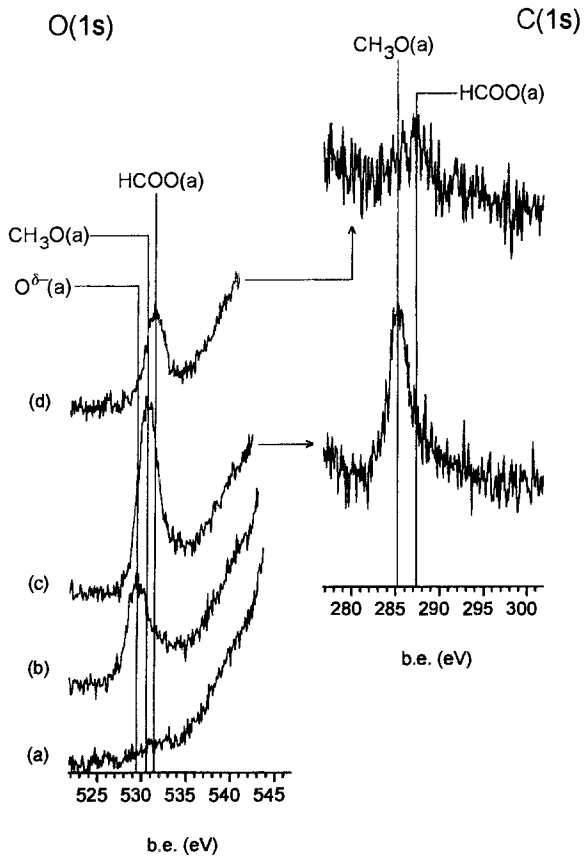

Fig. 10. O(1s) and C(1s) spectra illustrating formate formation from adsorbed methoxy: (a) clean Cu(pc) surface, (b) pre-exposed at 295 K to dioxygen – $\sigma_o = 0.21 \times 10^{15}$ cm^{-2}, (c) methoxy adlayer generated by exposure of (b) to methanol at 195 K – $\sigma_o = 0.46 \times 10^{15}$ cm^{-2}, (d) after heating the sample to 350 K – $\sigma_o = 0/18 \times 10^{15}$ cm^{-2}.

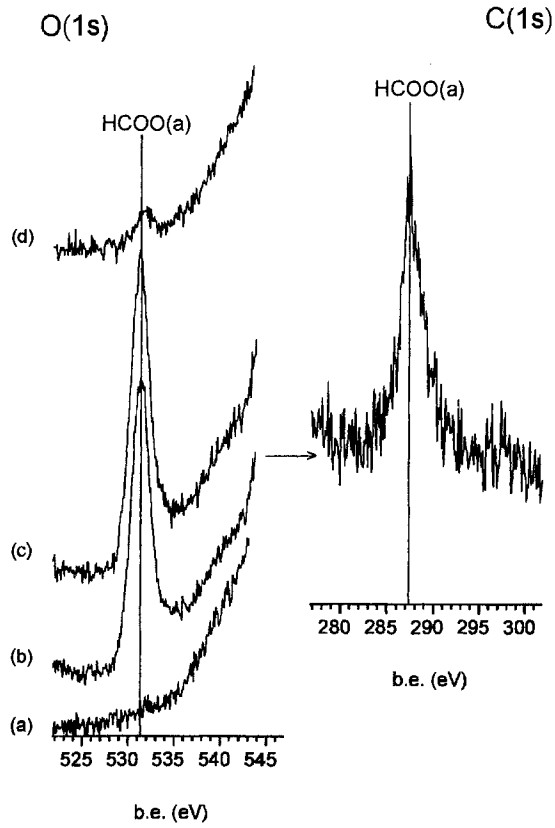

Fig. 11. O(1s) and C(1s) spectra for the interaction of formic acid with a Cu(pc) surface: (a) clean surface, (b) saturation coverage of formate ($\sigma_o = 0.68 \times 10^{15}$ cm^{-2}) after exposure to formic acid at 295 K, (c) after heating to 400 K ($\sigma_o = 0.73 \times 10^{15}$ cm^{-2}), (d) after heating to 473 K ($\sigma_o = 0.03 \times 10^{15}$ cm^{-2}).

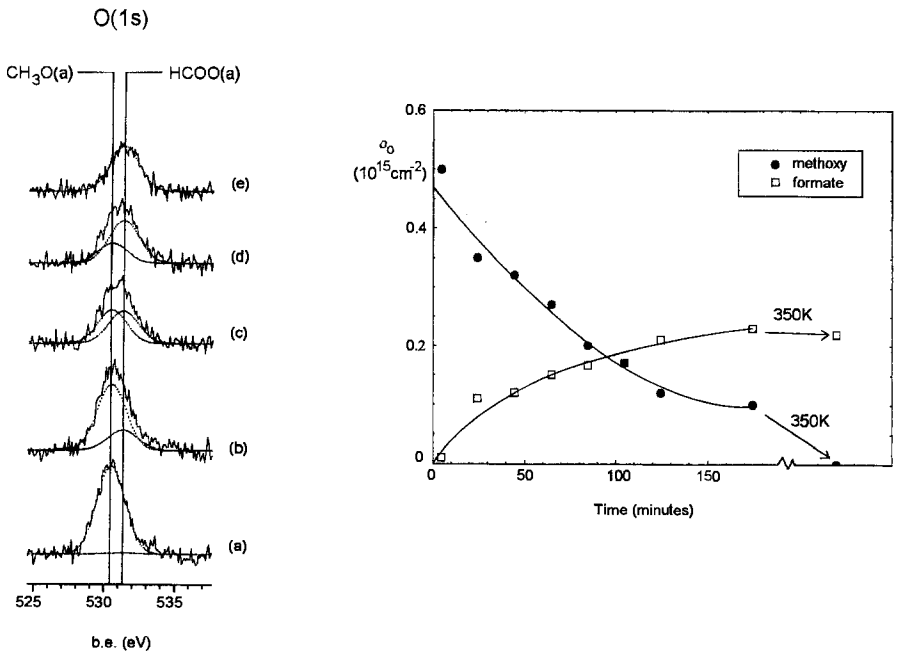

Fig. 12. Variation of methoxy and formate surface coverages as a function of time for a methoxy adlayer left in vacuo at 295 K. Also shown are some of the curve-fitted O(1s) spectra used to derive the respective surface concentrations, corresponding to times of: (a) 4.5 min, (b) 24.5 min, (c) 104.5 min, (d) 174.5 min, (e) after heating to 350 K.

a point we shall return to later. We note however that in some of the earliest studies reported by Roberts and Stewart [8] of methanol decomposition and oxidation, albeit at nickel and gold surfaces, methane was desorbed in significant quantities at 295 K. More recently, methane has been detected in an FTIR study of methanol synthesis over a Cu/SiO_2 catalyst [21]. The formate species at the copper surface are stable up to 350 K but decompose at 400 K to carbon dioxide and hydrogen which desorb from the surface,

$$HCOO(a) \rightarrow CO_2 + H(a) \quad (8)$$

$$2H(a) \rightarrow H_2(g) \quad (9)$$

It is the rate of the reaction, eq. (6), relative to the time scale of the experiment which determines whether a reaction stoichiometry of 1 : 1 or 2 : 1 is observed (figs. 7 and 8) – sequential or step-wise dosing involves a more prolonged experiment than when the total methanol exposure is achieved in a single dose. There is thus, in fact, no conflict between the molecular beam (MB) studies [1] on Cu(110) and our spectroscopic data for Cu(110)–O. MB data provide information relevant to the initial reaction step (eq. (5)) and thus at 300 K only the fast step, water desorption, is observed, whereas the quantitative XP data allow a more comprehensive understanding of both this step and any subsequent surface chemistry that might occur. In this context, a recent STM study [7] of methanol oxidation at Cu(110) surfaces concluded that the growth of methoxy islands was less rapid than expected from the MB studies, which is entirely consistent with our XPS observations. In the STM investigation, it was of course not possible to discriminate between methoxy and formate species, which we have shown are formed on Cu(110), albeit at a significantly slower rate than on Cu(pc).

The presence of surface formate in the MB and STM experiments could only be probed by post-reaction TPD, and conflicting observations have been reported [1,7]. This again may be a result of the rather slow rate of formate production on Cu(110), its concentration, and therefore detectibility by TPD, depending on how long after the initial exposure to methanol that TPD is performed. Formate production has also been observed in MB studies of methanol oxidation at a Cu–Pd alloy surface [22], in an FTIR investigation of methanol adsorption on $Cu/ZnO/SiO_2$ catalysts [21,23], and in a study of methanol synthesis on a Cu/SiO_2 catalyst [21].

We return now to the mechanism of formate production. The decrease in methoxy concentration in vacuo at 295 K and the rate of formate production levels off at a methoxy coverage of ca. 10% (fig. 12). The stability of these species is consistent with the reaction in eq. (7) being the route for formate formation since it requires two adjacent methoxy species. The "persistent" methoxy species are thus isolated species remaining after the pairwise elimination of methane. This also explains why on heating to 350 K desorption rather than formate production is favoured. The fact that desorption at 295 K not occur for these methoxys leads us to speculate that there are two adsorption sites for methoxy, one of which is associated with the desorption pathway leading to formaldehyde (eq. (6)), whilst the other leads to formate as the reaction product (eq. (7)). In the latter case, when this pathway is blocked, the methoxy species are stable at 295 K.

This model may be extended to explain the contrasting behaviours observed for methanol oxidation at Cu(110) and Cu(111) surfaces, since it is unlikely that two significantly different sites will exist on the latter surface. Indeed, evidence for two different types of methoxy species on the Cu(110) surface has been found in investigations aimed at elucidating their adsorption geometry. NEXAFS [24] and angle-resolved photoemission [20] studies first suggested the methoxy species was tilted, and X-ray photoelectron diffraction measurements [25] concluded that there were in fact two distinct methoxy species oriented differently with respect to the surface. On Cu(111), on the other hand, the consensus is that there is a single methoxy species oriented with its C–O axis normal to the surface [26–28]. The two species on Cu(110), with different angles of tilt to the surface, are thus identified with the two reaction pathways (1) and (2), and the two adsorption sites also existing on the polycrystalline surface. On Cu(111) neither reaction pathway is available to the vertically oriented methoxy species.

4. Conclusions

The mechanism of methanol oxidation at copper surfaces at 295 K has been shown to be more complex than previously thought. On Cu(110) and polycrystalline copper surfaces, the initial methoxy population, formed from the chemisorptive replacement of preadsorbed oxygen adatoms and the desorption of water molecules, decays via two reaction pathways: decomposition and evolution of formaldehyde, and the production of formate species through the elimination of hydrocarbons, possibly methane. The rate of formaldehyde production is similar for both Cu(110) and Cu(pc), whereas the rate of formate production is much faster for Cu(pc). At a Cu(111) surface neither reaction proceeds at a measurable rate.

Apparent discrepancies between our spectroscopic data and the results of molecular beam (MB) and temperature programmed desorption (TPD) investigations have been resolved by considering the rates of the two reaction pathways relative to the time scales of the various experimental techniques employed. Thus MB studies only "see" the initial fast step of water desorption, and the presence of formate will only be detected by TPD if the surface is left long enough for the surface con-

centration to become significant. The measured stoichiometry of the initial chemisorptive replacement reaction also depends on the time scale of the experiment, and we have shown that time-resolved surface spectroscopic studies are able to provide a more complete appreciation of the surface chemistry occurring than can the MB and TPD approaches.

It suggested that the two reaction pathways for methoxy at Cu(110) and Cu(pc) surfaces arise from the existence of two adsorption sites, with the methoxy species exhibiting different orientations with respect to the surface normal. On Cu(111) the methoxy is adsorbed with its C–O axis normal to the surface plane and is unreactive at 295 K.

Acknowledgement

We are grateful for support of this work from EPSRC and the European Commission–Brite Euram programme.

References

[1] C. Barnes, P. Pudney, Q. Guo and M. Bowker, J. Chem. Soc. Faraday Trans. 86 (1990) 2693.
[2] I.E. Wachs and R.J. Madix, J. Catal. 53 (1978) 208; Surf. Sci. 84 (1979) 375.
[3] I. Wachs and R.J. Madix, Surf. Sci. 76 (1978) 531.
[4] M. Bowker and R.J. Madix, Surf. Sci. 95 (1980) 190.
[5] F.M. Leibsle, S.M. Francis, R. Davies, N. Xaing, S. Haq and M. Bowker, Phys. Rev. Lett. 72 (1994) 2569.
[6] S.M. Francis, F.M. Leibsle, S. Haq, N. Xiang and M. Bowker, Surf. Sci. 315 (1994) 284.
[7] F.M. Leibsle, S.M. Francis, S. Haq and M. Bowker, Surf. Sci. 318 (1994) 46.
[8] M.W. Roberts and T.I. Stewart, in: *Chemisorption and Catalysis*, Institute of Petroleum Conference (Elsevier, Amsterdam, 1970) p. 16.
[9] M. Neurock, R.A. van Santen, W. Biemolt and A.P.J. Jansen, J. Am. Chem. Soc. 116 (1994) 6860.
[10] B. Afsin, P.R. Davies, A. Pashusky, M.W. Roberts and D. Vincent, Surf. Sci. 284 (1993) 109;
A.F. Carley, P.R. Davies, M.W. Roberts and D. Vincent, Topics Catal. 1 (1994) 35.
[11] A. Boronin, A. Pashusky and M.W. Roberts, Catal. Lett. 16 (1992) 345;
M.W. Roberts, J. Mol. Catal. 74 (1992) 11.
[12] A.F. Carley, PhD Thesis, University of Bradford (1980).
[13] A.F. Carley and M.W. Roberts, Proc. Roy. Soc. A 363 (1978) 403;
M.W. Roberts, Adv. Catal. 29 (1980) 55.
[14] B.A. Sexton, A.E. Hughes and N.B. Avery, Surf. Sci. 155 (1985) 366.
[15] M. Bowker and R.J. Madix, Surf. Sci. 102 (1981) 542.
[16] L.R. Dubois, T.H. Ellis, B.R. Zegrassi and S.D. Kevan, Surf. Sci. 172 (1986) 385.
[17] R.W. Joyner and M.W. Roberts, Proc. Roy. Soc. A 350 (1976) 107.
[18] B.E. Hayden, K. Prince, D.P. Woodruff and A.M. Bradshaw, Surf. Sci. 133 (1983) 589.
[19] A. Puschman, J. Haase, M.D. Crapper, C.E. Riley and D.P. Woodruff, Phys. Rev. Lett. 54 (1985) 2250.
[20] P. Hofmann and D. Menzel, Surf. Sci. 191 (1987) 353.
[21] G.J. Miller, C.H. Rochester and K.C. Waugh, Catal. Lett. 14 (1992) 289.
[22] M.A. Newton and M. Bowker, Catal. Lett. 21 (1993) 139.
[23] G.J. Millar, C.H. Rochester and K.C. Waugh, J. Chem. Soc. Faraday Trans. 88 (1992) 2257.
[24] M. Bader, A. Puschmann and J. Haase, Phys. Rev. B 33 (1986) 7336.
[25] E. Holub-Krappe, K.C. Prince, K. Horn and D.P. Woodruff, Surf. Sci. 173 (1986) 176.
[26] A.V. de Carvalho, M.C. Asensio and D.P. Woodruff, Surf. Sci. 273 (1992) 381.
[27] Ph. Hofmann, K.-M. Schindler, S. Bao, V. Fritzsche, D.E. Ricken, A.M. Bradshaw and D.P. Woodruff, Surf. Sci. 304 (1994) 74.
[28] M.A. Chesters and E.M. McCash, Spectrochim. Acta 43A (1987) 1625.