

## General Discussion

**Dr. Davies** opened the discussion of Prof. Freund's paper: Do the oxygen studies identified by the IR peaks at 965 and 990  $\text{cm}^{-1}$  ( $^{16}\text{O}_2$ ) in Fig. 3 of your paper<sup>1</sup> interconvert, and is there any difference in the interaction of these two species with ethene?

1 B. Dillmann, F. Rohr, O. Seiferth, G. Klivenyi, M. Bender, K. Homann, I. N. Yakovkin, D. Ehrlich, M. Bäumer, H. Kühlenbeck and H.-J. Freund, *Faraday Discuss.*, 1996, **105**, 295.

**Prof. Freund** responded: At 90 K only the feature at 990  $\text{cm}^{-1}$  is detectable while upon heating, the feature at 965  $\text{cm}^{-1}$  appears, indicating interconversion. However, we have not checked what happens upon cooling the surface again.

We have no indication for any interaction between adsorbed  $\text{O}_2$  and coadsorbed ethene.

**Prof. Goodman** asked: Following the adsorption of  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ , molecular desorption of  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$  is observed with little oxygen scrambling. The reflection-adsorption infrared study (RAIRS) results, however, show appreciable dissociation of  $\text{O}_2$ . Do you have an idea of the relative amounts of  $\text{O}_2$  that desorb molecularly *vs.* the amount that dissociates?

**Prof. Freund** responded: On the basis of the presented thermal desorption study (TDS) and RAIRS results this is difficult to estimate. The reasons for this are two-fold: firstly, the dissociatively adsorbed oxygen does not desorb before the film loses appreciable amounts of oxygen from the lattice and secondly, the dynamic dipole moments of adsorbed  $\text{O}_2$  and O are considerably different rendering an evaluation of adsorbed quantities impossible at present.

**Prof. Somorjai** asked: What is the surface structure of the  $\text{Cr}_2\text{O}_3$  surface? Have there been low-energy electron diffraction (LEED) surface crystallography studies performed on this surface?

Is it possible that ethene adsorption reduces  $\text{Cr}_2\text{O}_3$  in such a way that  $\text{Cr}^{2+}$  ions are produced.  $\text{Cr}^{2+}$  ions are thought to catalyse ethene polymerization and you indicated that polymerization was observed. The effect of oxygen coadsorption that reduces the ethene coverage could then be explained as due to the preservation of the  $\text{Cr}^{3+}$  oxidation state of the surface metal ions.

**Prof. Freund** responded: We have published an LEED *I/V* study determining the surface structure.<sup>1</sup>

We had thought originally<sup>2</sup> that  $\text{Cr}^{2+}$  exists at the surface. This was based on the analysis of energy loss spectroscopy (ELS) data of surface electronic d–d excitations. The observed excitation energies were compatible with optical excitation energies in coordination compounds containing formally  $\text{Cr}^{2+}$  ions. Later, we realized that the observed excitation energies are also compatible with  $\text{Cr}^{3+}$  residing in a ligand field of particular shape and strength. At present, we think that the d–d excitations are indicative of 3 d-electrons. Still, the overall charge on Cr could be 2+ due to the possible involvement of s-electrons in a partly covalent Cr–O bond in the surface.<sup>3,4</sup>

1 F. Rohr, M. Bäumer, H.-J. Freund, A. Mejias, V. Staemmler, S. Müller, L. Hammer and K. Heinz, *Surf. Sci. Lett.*, 1997, **372**, L281.

2 C. Xu, B. Dillmann, H. Kühlenbeck and H.-J. Freund, *Phys. Rev. Lett.*, 1991, **67**, 3551.

- 3 M. Bender, D. Ehrlich, I. N. Yakovkin, R. Rohr, M. Bäumer, H. Kühlenbeck and H.-J. Freund, *J. Phys.: Condens. Matter*, 1995, 7, 5289.
- 4 J. A. Mejias, V. Staemmler and H.-J. Freund, *Chem. Phys. Lett.*, in preparation.

**Prof. Zecchina** asked: The chromyl species formed on the (0001) face of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> should form an array of parallel oscillators. Lateral dynamic interactions are expected, which should be coverage dependent. Did you observe any significant change of the  $\nu(\text{Cr}=\text{O})$  frequency with coverage?

**Prof. Freund** responded: We do observe small shifts as a function of coverage, *i.e.* upon heating the surface.

Whether these shifts are caused by dipole couplings is not clear because the distance of the chromyl group is large, as judged by the separation of Cr ions in the clean surface.

**Prof. Sheppard** asked: I now understand why (previously) you asked me why absorption bands in IR spectra can vary in relative intensity. One reason can be geometrical and I notice from your diagram that the surface of your Cr<sub>2</sub>O<sub>3</sub> crystal has different periodicities in mutually perpendicular directions. For the surface of an insulator the conventional grazing-incidence geometry for RAIRS can, in principle, only probe dipole changes perpendicular to the surface and in one direction parallel to the surface. I notice that C<sub>2</sub>H<sub>4</sub> forms a more weakly bound species that is thought to be randomly oriented because a C–H stretching mode, which has thus become active, shows in fact only one of the two mutually perpendicular IR active C–H stretching modes. I suspect, therefore, that this more weakly bound species retains some direction of preferred orientation on the oxide surface.

**Prof. Sheppard** subsequently communicated: In my previous comment on the RAIRS spectrum of the adsorbed ethene I had not recalled that modes of vibration that have dipole changes perpendicular to the surface remain strongly favoured for your oxide-on-metal system. This is principally because of the presence of the underlying metal and the consequent operation of the metal surface selection rule. As a result a more specific deduction can be made concerning the orientation of the weakly adsorbed ethene species relative to the surface.

The observed absorption at 2980 cm<sup>−1</sup> is clearly from the  $b_{3u}$   $\nu\text{CH}_2$  s-mode which has its vibrational dipole change along the C–C direction. However, the  $b_{2u}$   $\nu\text{CH}_2$  as-mode, with its dipole change in the molecular plane and perpendicular to the C–C direction (expected near 3105 cm<sup>−1</sup>) is missing. These two considerations (together with the continued observation of the out-of-plane CH<sub>2</sub> wagging mode near 1017 cm<sup>−1</sup>) show that the plane of the adsorbed ethene molecule is tilted from parallelism with respect to the surface by rotation about the axis within the molecular plane that is perpendicular the C–C direction.

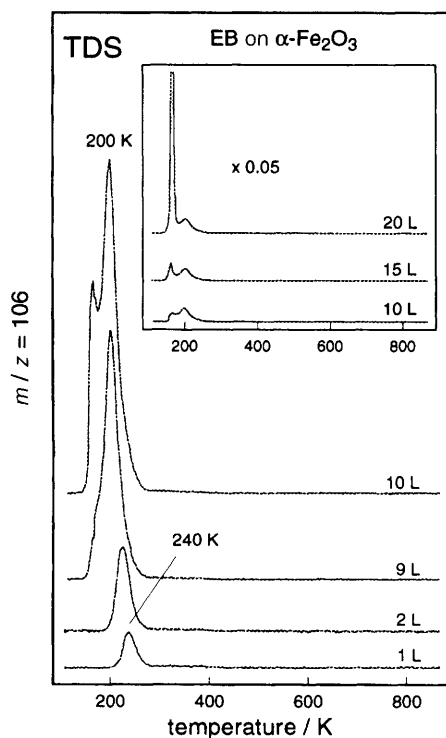
**Prof. Freund** responded: We have not varied the azimuthal angle in our scattering experiment. At present, we feel that on the basis of our limited signal-to-noise ratio the absence of a band cannot be confirmed with certainty. We appreciate the comments.

**Dr. Weiss** commented: The adsorption of oxygen and ethene onto the Cr<sub>2</sub>O<sub>3</sub>(0001) surface is studied by several surface science techniques. The atomic structure of this polar surface was determined by a dynamic LEED intensity analysis. It forms an unreconstructed chromium-terminated structure where only half of all bulk chromium sites are occupied in the top layer, which reduces the surface charge and therefore stabilizes this polar surface. Strong relaxations involving the first four interlayer distances were observed. Two adsorption states below room temperature were observed by

temperature-programmed desorption (TPD) for ethene on this surface. I would like to compare these results to our results obtained on iron oxide surfaces.

In order to gain insight into the chemistry on oxide surfaces we grow thin epitaxial iron oxide films onto Pt(111) substrates. Variation of the oxygen partial pressure and of the number of iron deposition–oxidation cycles allows us to prepare well ordered FeO monolayer films as well as Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> multilayer films, the latter by high pressure oxidation.<sup>1</sup> All three oxide films have different bulk and surface structures, and therefore we can study the influence of the composition and surface structure on the chemistry and catalytic activity of these films. As iron oxide-based catalysts are used for styrene synthesis, we study the adsorption and dehydrogenation of ethylbenzene to styrene on these films.

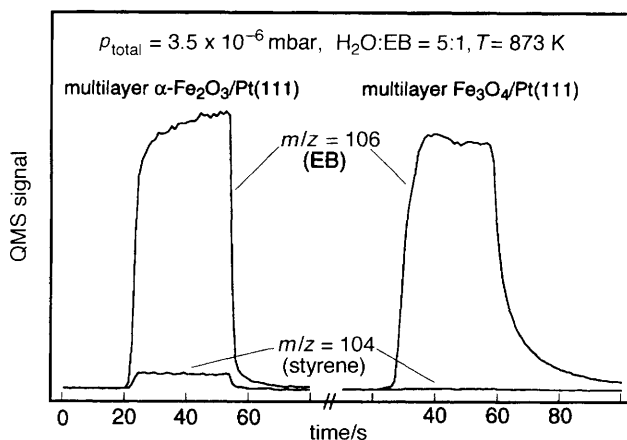
Fe<sub>3</sub>O<sub>4</sub>(111) forms an iron-terminated surface structure as determined by an LEED intensity analysis.<sup>2</sup> Two different iron terminations separated by steps were observed in a single crystal STM study.<sup>3</sup> Recent LEED intensity calculations indicate an oxygen- or OH-terminated surface structure of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) haematite surface, which is very different from the Cr<sub>2</sub>O<sub>3</sub>(0001) surface, although both oxides have the same corundum crystal structure. Also, the interlayer relaxations of the haematite surface are smaller which might be due to different ionicities in these oxides. As for ethene on Cr<sub>2</sub>O<sub>3</sub>(0001), we find two adsorption states below room temperature for ethylbenzene on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) (see Fig. 1). The first desorption peak occurs at  $T = 240$  K and shifts to 200 K with increasing exposure, the second desorption peak occurring at higher exposures is due to condensed ethylbenzene multilayers. Very similar behaviour is observed



**Fig. 1** TPD spectra of ethylbenzene (EB) adsorbed on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001). 1 L (langmuir) =  $10^{-6}$  Torr s.

on the  $\text{Fe}_3\text{O}_4(111)$  surface. However, the catalytic behaviour of these films differs considerably. No ethylbenzene dehydrogenation is observed in a water-ethylbenzene mixture on the  $\text{Fe}_3\text{O}_4(111)$  film at  $T = 873$  K, whereas on the  $\alpha\text{-Fe}_2\text{O}_3(0001)$  film we observe styrene production under these conditions, as can be seen in Fig. 2. Depending on the nature of the active sites, this might be caused by the different surface structures on these oxide films or by different defect structures, which is currently under scrutiny. Also the electronic structures of the two oxide films differ slightly as observed by photoelectron and X-ray absorption spectroscopy,<sup>4</sup> and the number and nature of basic surface oxygen anions might also influence the catalytic film activities. It would be interesting to compare the dehydrogenation chemistry of the  $\alpha\text{-Fe}_2\text{O}_3(0001)$  surface to the one of  $\text{Cr}_2\text{O}_3(0001)$ .

- 1 W. Weiss, M. Ritter and R. Schlögl, *Surf. Sci.*, in press.
- 2 W. Weiss, A. Barbieri, M. A. VanHove and G. A. Somorjai, *Phys. Rev. Lett.*, 1993, **71**, 1848.
- 3 A. R. Lennie, N. G. Condon, F. M. Leibsle, P. W. Murray, G. Thornton and D. J. Vaughan, *Phys. Rev. B*, 1996, **53**, 10244.
- 4 Th. Schedel-Niedrig, W. Weiss and R. Schlögl, *Phys. Rev. B*, 1995, **52**, 17449.



**Fig. 2** Catalysis experiment displaying the molecular ethylbenzene (EB) and styrene signals measured on  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  multilayer films

**Prof. Goodman** asked: In the coadsorption experiment of ethene and oxygen, did you observe any oxygenated products?

**Prof. Freund** responded: We have not looked in detail but at present there is no indication of oxygenated products.

**Prof. Thornton** asked: Have you considered the possibility of two terminations of  $\text{Cr}_2\text{O}_3(111)$ , similar to that observed for  $\text{Fe}_3\text{O}_4(111)$ ?<sup>1</sup>

- 1 A. R. Lennie, N. G. Condon, F. M. Leibsle, P. W. Murray, G. Thornton and D. J. Vaughan, *Phys. Rev. B*, 1996, **53**, 10244.

**Prof. Freund** responded: It is unlikely that  $\text{Cr}_2\text{O}_3$  is partly metal- and partly oxygen-terminated due to electrostatic arguments. Of course, we expect terraces on the surface but I would expect metal termination in all cases.

**Prof. Chesters** said: Could I ask for further clarification on the interpretation of your IR spectra of adsorbed ethene? You state that the dielectric response of your surface is

such that you are effectively governed by the metal surface selection rule and this is why the C–H stretching bands are absent from the spectrum of the more strongly adsorbed ethene.

For the more weakly adsorbed ethene which you propose to be randomly oriented I would expect to see both IR active C–H stretching bands in your spectrum. I would also expect the frequency of the C–H out-of-plane deformation to be close to that in the solid or liquid phase, *i.e.*  $950\text{ cm}^{-1}$  as is found for very weakly adsorbed ethene on silver surfaces. I would therefore suggest that your weakly adsorbed ethene species does show evidence of preferred orientation and is probably weakly chemisorbed rather than physisorbed.

**Prof. Freund** responded: This is a possibility and we appreciate the comment. However, we know from TDS that there is a weakly and a more strongly held species.

**Prof. Zecchina** asked: How is the IR spectrum of CO adsorbed on the (0001) face? Is it similar to that observed on neutral faces of polycrystalline samples described in my contribution (ascribed to linear  $\text{Cr}^{3+}$ –CO species where the  $\text{Cr}^{3+}$ –CO bond is weak and polar) or do you observe entirely new features?

**Prof. Freund** responded: My comments relating to this question are covered in my remarks on Prof. Zecchina's paper (p. 182).

**Dr. Ge** asked: Does chromia ( $\text{Cr}_2\text{O}_3$ ) film show magnetic character? If yes, how do the magnetic properties affect the adsorption of  $\text{O}_2$ , or in general, chemisorption of molecules on the surface?

**Prof. Freund** commented: We have no direct evidence for magnetic character. However, we have speculated that the phase transitions observed<sup>1</sup> may be connected with surface magnetism. We note that the phase transition disappears upon  $\text{O}_2$  adsorption.

<sup>1</sup> M. Bender, D. Ehrlich, I. N. Yakovkin, R. Rohr, M. Bäumer, H. Kühlenbeck and H.-J. Freund, *J. Phys.: Condens. Matter*, 1995, 7, 5289.

**Prof. Sir John Meurig Thomas** commented: The STM micrographs shown by H.-J. Freund and by D. W. Goodman prompt one to recall the work of Swiss physicists (in Basel)<sup>1</sup> some decades ago in which they investigated the influence of particle size of Au on the melting point, which was measured by delicate electron diffraction. (By warming the 'holey' carbon film on which the Au was deposited, the conversion of sharp diffraction rings to diffuse ones on melting could be readily recorded.) Remarkably, they found that small particles of Au (*ca.* 10 Å diameter) had exceptionally low melting points, close to 350 K as I recall.

<sup>1</sup> P. Buffat, Thesis, Ecole Polytechnique Fédérale de Lausanne, No. 252, Switzerland, 1976.

**Prof. Goodman** responded: Yes, indeed, there have been several examples in the literature detailing reduced melting points in small metal clusters. Obviously the reduced coordination at the surface of small clusters that contributes to the observed lower sublimation energies is directly related to those factors that alter the melting points. The structural modifications and the nature of the bonding within small clusters is a subject of considerable experimental and theoretical efforts. The sublimation energies that we have measured should be helpful in conjunction with future theoretical efforts along these lines.

**Prof. Thornton** asked: Our work on potassium adsorption on  $\text{TiO}_2(100)$  suggests that at elevated temperature oxygen is abstracted from the bulk to form<sup>1</sup> potassium

oxide. In your thin film oxide surface you have a limited supply of oxygen. Have you investigated the dependence of the sodium species on film thickness?

1 A. G. Thomas, P. J. Hardman, C. A. Muryn, H. S. Dhariwal, A. F. Prime, G. Thornton, E. Roman and J. L. de Segovia, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3569.

**Prof. Freund** responded: We have not systematically studied this question, but we know that in the case of very thin films problems of film rupture may occur. We have therefore used films thick enough so that these problems do not occur.

**Prof. Kasemo** said: I have a very specific question about your sodium 2p spectra and their interpretation, which I then follow with a more general question about spectroscopy on metal clusters/atoms on thin oxides on metal substrates. The first question concerns your interpretation of the 'abnormally' high Na 2p binding energy as due to neutral Na atoms. Would you not expect the highest binding energy to be due to an ionic species? If the same argument that you apply for the Na atom, placed on the surface, was instead applied to an  $\text{Na}^+$  ion, you would get an even higher binding energy. More generally: How is the spectroscopy of atoms/ions/metal clusters influenced and possibly complicated by the fact that the analysed species are interacting with the underlying metal (image interaction, polarization effects *etc.*)?

**Prof. Goodman** responded: This is a very interesting point and question. Because Prof. Freund has carried out recent experiments to address just this point, I will defer to him and allow him to describe the implications of his work with respect to this question.

**Prof. Freund** commented to Prof. Kasemo: In our study we assign metallic sodium, an ionic sodium species and a third species, which we speculate is not ionic. The assignment is based on chemical shifts in photoelectron and Auger spectra. We have used both to clarify the influence of final state effects.

The chemical shifts of the metallic and ionic species (also responsible for the change in work function) are compatible with literature data including our own. The reference data include powder samples, single crystals and thin films. This is a hint that there is not a peculiar effect due to the presence of the metal support. In fact, we know that there is a very small effect of the order of 100–200 meV from our work on metal deposits on thin alumina films.<sup>1,2</sup>

As to the assignment of the third species we note that atomic Na has the highest Na 1s binding energy, metallic Na the lowest; ionic Na 1s is intermediate, as shown in Fig. 12 of our paper.<sup>3</sup>

As far as the Auger lines are concerned, we have explained their relative positions in the paper. We are not certain, of course, that the third species is 'neutral' but its binding energy is consistent with this assignment and the ionic species does not necessarily have to have the highest binding energy. Obviously, final state relaxations dominate the shifts in the present systems.

1 J. Libuda, M. Franck, A. Sendek, S. Andersson, P. A. Brühwiler, M. Bäumer, N. Håkansson and H-J. Freund, to be published.

2 J. Libuda, PhD thesis, University of Bochum, 1996.

3 B. Dillmann, F. Rohr, O. Seiferth, G. Kuvenyi, M. Bender, K. Homann, I. N. Yakovkin, D. Ehrlich, M. Bäumer, H. Kühlenbeck and H-J. Freund, *J. Chem. Soc., Faraday Trans.*, 1996, **105**, 295.

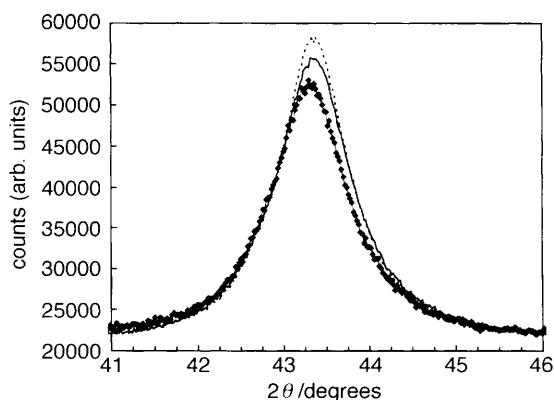
**Prof. Joyner** opened the discussion of Dr. Schroeder's paper: It is pleasing that the surface sensitivity of the total electron-yield method (TEY) is now clarified and that it is recognized as a quasi-bulk technique. Most people will be comfortable with this conclusion. It is also useful to be told that the copper oxidation results reported earlier by this group, and which lead to a conclusion of high surface sensitivity resulted from an experimental artifact.



My question relates to the oxidation of copper in methanol synthesis catalysts. You conclude that the main evidence for interaction with a small dose of oxygen ( $10^8$  L†) is in a total reduction of EXAFS amplitude. For me, the simplest explanation is that this is an artifact of the TEY method. Has this observation therefore, been checked in transmission mode?

**Dr. Schroeder** responded: Our paper acknowledged that there is some uncertainty about the accuracy of the absolute (XAFS) amplitude in total electron-yield (TEY) data of particles. However, reversible changes following reactive treatments cannot be caused by an artifact, especially since the actual measurement conditions (gas composition *etc.*) were all strictly identical. The results have also been reproduced several times. Nevertheless, to corroborate that the state of the sample changes significantly we present *in situ* X-ray diffraction (XRD) data taken after the same treatments as applied during the XAFS studies (Fig. 1). It is seen that there is a loss (*ca.*  $8\% \pm 2\%$ ) and a gain (*ca.*  $12\% \pm 2\%$ ) in intensity of the Cu metal (111) reflex during oxidation and re-reduction, respectively (there is also some sharpening of the diffraction line due to sintering during reduction, as well as a small, reversible shift of the peak position which will be discussed elsewhere<sup>1</sup>). The *in situ* XRD data thus prove that the oxygen exposure converts *ca.* 10% of the Cu into an oxidised reaction product. The magnitude of this XRD-observed metal loss/gain agrees well with the XAFS amplitude variations reported in our paper, suggesting that the variations in the XRD and XAFS data share their origin, namely removal of a fraction of metallic Cu by incorporation into an oxidised phase. The XAFS is quite insensitive to contributions of low-Z backscatterers (which have intrinsically small XAFS amplitude) against the background of scattering contributions from higher-Z atoms. This problem, which has been known to XAFS practitioners for quite some time, is so seminal for the interpretation of catalyst data that we wish to demonstrate it more conclusively with a straightforward modelling study.

We first generated model absorption spectra by superposition of the normalised K-edge spectra of Cu and Cu<sub>2</sub>O [*cf.* Fig. 4(b) in our paper] in varying ratios. These model data were then analysed exactly like the catalyst data. In Fig. 2 we present the resulting moduli of the Fourier transforms of the  $k^1$ -weighted EXAFS functions for Cu : Cu<sub>2</sub>O ratios of 10 : 0, 9 : 1 and 8 : 2. It is seen that the presence of Cu<sub>2</sub>O results



**Fig. 1** *In situ* XRD analysis [only the Cu(111) line is shown] of the effect of small oxygen exposure on the reduced catalyst. (—) Initial reduction for 5 min at 250 °C in 100% H<sub>2</sub>, *T* ramp: 20 °C min<sup>-1</sup>. (—◆—) Air-exposed ( $10^8$  L of O<sub>2</sub> at room temperature). (---) Sample re-reduced for 5 min at 250 °C in 100% H<sub>2</sub>, *T* ramp: 20 °C min<sup>-1</sup>.

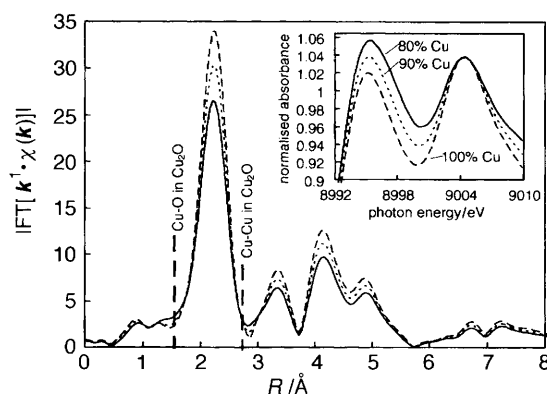
† 1 L (langmuir) =  $10^{-6}$  Torr s.

**Table 1** Results of an EXCURV92 single-scattering fitting analysis for EXAFS data of the Cu K-edge model spectra (100% Cu, 90% Cu/10% Cu<sub>2</sub>O, 80% Cu/20% Cu<sub>2</sub>O) discussed in the text

	100% Cu	90% Cu/10% Cu <sub>2</sub> O		80% Cu/20% Cu <sub>2</sub> O	
		without O-shell	with O-shell	without O-shell	with O-shell
$S_0^2$	0.83(3)	0.77(3)	0.76(3)	0.71(3)	0.69(3)
$N_1 \cdots N_5$			12/6/24/12/24(fixed)		
$R_1/\text{\AA}$	2.540(3)	2.541(3)	2.544(3)	2.542(3)	2.547(3)
$R_2/\text{\AA}$	3.572(8)	3.574(8)	3.579(8)	3.573(9)	3.583(9)
$R_3/\text{\AA}$	4.443(6)	4.446(7)	4.453(7)	4.448(8)	4.460(7)
$R_4/\text{\AA}$	4.919(7)	4.921(7)	4.927(7)	4.921(8)	4.932(8)
$R_5/\text{\AA}$	5.79(1)	5.79(1)	5.80(1)	5.79(2)	5.81(2)
$2\sigma_1^2$	0.0154(8)	0.0158(8)	0.0158(8)	0.0163(9)	0.0161(9)
$2\sigma_2^2$	0.018(2)	0.018(2)	0.018(2)	0.019(2)	0.018(2)
$2\sigma_3^2$	0.021(1)	0.022(1)	0.021(1)	0.023(2)	0.022(2)
$2\sigma_4^2$	0.010(1)	0.010(1)	0.010(1)	0.011(2)	0.011(2)
$2\sigma_5^2$	0.028(4)	0.028(4)	0.028(4)	0.028(4)	0.030(4)
$E_t/\text{eV}$	-9.1(4)	-9.4(4)	-10.0(4)	-9.6(5)	-10.6(5)
$R_0/\text{\AA}$	—	—	1.94(3)	—	1.93(2)
$2\sigma_0^2$	—	—	0.02(fixed)	—	0.02(fixed)
$N_0$	—	—	0.8(2)	—	1.0(2)
R-factor	21.2	21.7	21.0	23.0	21.0

Please see Table 1 in our Discussion paper (p. 327) for definition of variables.

almost exclusively in the disappearance of Cu metal EXAFS amplitude. There is a tiny gain of intensity where backscattering from the nearest O- and Cu-shells in Cu<sub>2</sub>O is expected [the position and intensity of the first two coordination shells in pure Cu<sub>2</sub>O are indicated in Fig. 2 (---)], but the unequivocal identification of such small changes would be very difficult if the sample structure was not known *a priori*. The inset of Fig. 2 demonstrates that the presence of Cu<sub>2</sub>O is more evident in the X-ray absorption near-edge structure (XANES) region (note the qualitative similarity to the changes observed for the Cu catalyst, *cf.* Fig. 5 in our paper). We also provide a table of fitting results for the EXAFS functions of the simulated spectra. The trends in the results resemble those



**Fig. 2** Moduli of the Fourier transforms of the model spectra discussed in the text. The inset contains a part of the XANES region of the pre-edge subtracted, normalised spectra. (—), 100% Cu; (·····), 90% Cu/10% Cu<sub>2</sub>O; (---), 80% Cu/20% Cu<sub>2</sub>O.



observed for the catalyst data in all important aspects, *i.e.*, (i) the presence of oxidised Cu induces significant changes only in the overall amplitude parameter  $S_0^2$ , (ii) for the spectra containing  $\text{Cu}_2\text{O}$  contributions, inclusion of an oxygen shell improves the fit quality significantly, but the Debye–Waller factor of the oxygen shell has to be fixed to avoid erroneous fit optimisation with unphysically high coordination numbers and (iii) the radial position of the fitted oxygen shell optimises consistently above 1.90 Å, significantly higher than expected for  $\text{Cu}_2\text{O}$  (1.85 Å). In conclusion, even if 20% of the total Cu content resides in ordered, stoichiometric  $\text{Cu}_2\text{O}$ , the unequivocal identification of oxygen backscatterers presents great difficulties. Note that a separate oxide phase was not evident in the XRD pattern of the oxidised catalyst. This indicates that the oxidised Cu is present in a considerably disordered and/or non-stoichiometric phase, for which the XAFS amplitudes are likely to be even lower than in the ordered  $\text{Cu}_2\text{O}$  assumed for our model spectra.

This discussion demonstrates that our preliminary interpretation of the XAFS amplitude variations in terms of Cu conversion from the metallic to some oxidised state is plausible; the changes are unlikely to be due to an experimental artifact. We thus decided against taking comparative transmission measurements (which would, because of the high Cu loading of the catalyst, also be prone to some doubt because of the possibility of artificial distortions due to ‘thickness effects’).

1 S. L. M. Schroeder, G. D. Moggridge, R. M. Lambert, T. Rayment, H. Werner and R. Schloegl, to be published.

**Prof. Thornton** commented: I note that you have analysed the EXAFS data using single scattering code. Multiple scattering code is now available. Have you attempted to analyse your data using this method?

**Dr. Schroeder** replied: We routinely compare our single-scattering (SS) analysis with results of multiple-scattering (MS) calculations to identify possible oversights due to the neglect of MS paths. For the extended fine-structure results presented in our paper, improved fits to the experimental data can indeed be obtained by considering MS paths. However, the MS analysis yielded no important additional insight, especially from the viewpoint of catalytic chemistry, so that only the SS analysis was presented. A full MS analysis is currently being carried out for the XANES of the Cu particles in the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst and other near-edge data of dispersed materials. Because of its greater transparency, comprehensiveness and versatility, we use the FEFF code<sup>1</sup> rather than EXCURV92<sup>2</sup> for MS calculations. For SS calculations, results obtained by both codes are only rarely different, but we prefer the SS mode of EXCURV92 because of its better inbuilt statistical tests for characterising the fit quality.

1 S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers and M. J. Eller, *Phys. Rev. B*, 1995, **52**, 2995.

2 N. Binsted, J. W. Campbell, S. J. Gurman and P. C. Stephens, *SERC Daresbury Laboratory EXCURV92 Program*, 1991.

**Prof. Freund** asked: Would it be possible to also use partial electron-yield detection to become even more surface sensitive, and how does this interfere with changing compositions in the gas phase?

**Dr. Schroeder** responded: Yes, our ongoing work has shown that partial electron-yield detection is now a practical possibility using gas microstrip detector (GMSD) technology. The underlying principle is that of gas-proportional detection, *i.e.* strong electric fields are applied to induce electron avalanches in the gas phase. Each electron emitted from the surface is detected as a strong charge pulse, the intensity (‘height’) of each being proportional to the kinetic energy of the trigger electron. *Via* pulse height analysis, an electron energy spectrum with *ca.* 10–15% resolution can thus be obtained,

which, in conjunction with sufficiently fast counting electronics, allows the selection of partial yields. As you suggest, changes in the gas compositions indeed have a detrimental effect on this technique. This is because the stability of the detector calibration relies on constant amplification characteristics of the gas phase throughout the whole spectrum acquisition, so that gas compositions and pressures must be maintained with high precision. Furthermore, at the high voltages applied in proportional detectors, many gases are prone to electrical breakdown due to spontaneous discharge. Proportional detection is therefore unlikely to be very useful as an *in situ* technology for studies under reaction conditions. The great value of GMS detection is that it achieves excellent signal-to-noise ratios. Good spectra have been obtained on timescales similar to those of conventional XAFS experiments, even with photon fluxes little above those of some laboratory *bremstrahlung* sources. GMS detection might therefore open up new possibilities for laboratory XAFS studies of thin overlayers.

Finally, I would like to add that the maximum surface sensitivity of electron-yield detection is dictated by the inelastic mean free path of the Auger electrons, which can be, especially for XAFS measurements in the keV range, considerably higher than the effective depth probed with X-ray incidence below the critical angle for total internal reflection. If sufficiently large, planar samples are available, measurements in total-reflection geometry (RefleXAFS) are a superior alternative to proportional detection. Furthermore, the TEY (and/or the fluorescence-yield) can be used to probe the RefleXAFS signal. True *in situ* measurements are therefore possible.

**Prof. Bowker** asked: You showed a spectrum for iodine adsorbed on Au(111) in which you could identify the edge, although the data acquisition was laborious. A problem in interpretation is the poor signal : noise ratio; what are the prospects for significant improvement in this ratio, and do you feel the technique will be really useful for monolayer studies *in situ*?

**Dr. Schroeder** responded: As concluded in our paper, fluorescence-yield measurements with a good solid-state detector are generally more suited to *in situ* surface extended X-ray absorption fine-structure (SEXAFS) studies of monolayers because of an intrinsically better signal-to-background ratio. Proportional detection and total X-ray reflection geometries are two practical ways to improve the signal-to-background quality of electron-yield experiments, but it is difficult to predict whether these improvements alone will enable *in situ* electron-yield SEXAFS studies in the future. However, developments in spectrometer technology should also be awaited. Especially if the intrinsic background levels of monochromators and X-ray focusing optics could be lowered, *in situ* electron-yield detection might become a more competitive alternative to fluorescence measurements on monolayers. It should also be stressed that our SEXAFS data were obtained using a spectrometer which was not optimised for this type of experiment. The recently published TEY SEXAFS data from Brookhaven<sup>1</sup> (discussed in our paper) look considerably better than ours.

<sup>1</sup> I. H. Song, B. Rickett, P. Janavicius, J. H. Payer and M. R. Antonio, *Nucl. Instrum. Methods A*, 1995, **360**, 634.

**Prof. Goodman** asked: Given the time, effort and resources that you have invested in carrying out these impressive set of explanatory experiments, and with the experience that you have acquired in seeing them to completion, would you recommend that myself and others invest in setting up such capabilities?

**Dr. Schroeder** responded: Yes, especially in view of the fact that the investment costs are only a small fraction of those required by many other spectroscopies [in particular those operating in ultra-high vacuum (UHV)]. *In situ* cells suitable for TEY XAFS

studies of catalysts are easily designed and built. Provisions must be made only for an X-ray entrance window, gas in- and out-lets, sample support, a biased collector foil/wire, and small electrical feedthroughs. Temperature variation can be achieved either by heating the sample support or by designing an externally heated isothermal cell. Of course, in designing such cells and in applying the technique the constraints discussed in our paper must be kept in mind. Especially the problems encountered in measurements on submonolayers are a discouraging result to surface scientists who model catalytic reactions under UHV conditions. However, our conclusions also bear out that TEY XAFS is a useful spectroscopic tool for (i) the large community of scientists and engineers studying 'real-world' catalysts, and (ii) the fast-growing group of researchers working with model catalysts under realistic reaction conditions. Particularly from the latter, this Discussion has seen several aspects of catalysis research which could almost certainly benefit from complementary measurements by *in situ* TEY XAFS. Examples include the morphology changes in nanofabricated model catalysts under reaction conditions, the reaction-induced recrystallization processes at well defined surfaces or the lattice dynamics and electronic structure changes underlying the concurrent growth of overlayers and incorporation of dopant species into model oxide systems, all areas where *in situ* TEY XAFS offers an opportunity to obtain detailed structural and electronic information under realistic reaction conditions.

By combination with an efficient fluorescence-yield detector (nowadays standard equipment at many non-UHV XAFS beamlines), such studies can be extended to include submonolayer amounts of the catalytically active materials. Finally, the TEY technique is certainly not limited to studies of model catalysts. Phase transformations during the preparation of dispersed catalysts are an obvious area where additional insight could be obtained with TEY XAFS.

**Prof. Kasemo** asked: Is there an optimum pressure regime for a specific type of measurement? I imagine that the gas-phase related effects can be very different in different pressure regimes, *e.g.* due to electron mean free path effects.

**Dr. Schroeder** responded: In our experience, the choice of the gas and its pressure are mostly an issue when the gas is strongly X-ray absorbing, as, *e.g.*, Ar. To overcome the ensuing problem of insufficient X-ray penetration, suitable detector cells with minimised X-ray paths can be constructed. There is not really an 'optimum' pressure range, as illustrated by the fact that we have performed TEY measurements in pressure regimes from UHV up to at least 40 atm. Only when the electron mean free path becomes long enough to allow additional impact ionization of gas particles due to field acceleration, the TEY signal response tends to be somewhat unstable because small pressure variations can then lead to relatively large fluctuations in the gas amplification characteristics. Typical field strengths employed for TEY detection are *ca.* 100 eV (some workers employ voltages up to 1000 V, but we have repeatedly found that this is unnecessary), for which the unstable region arises mostly in the pressure regime of 'bad' vacuum, *i.e.*, *ca.*  $10^1$ – $10^{-3}$  mbar. For lower pressures, the collision mean free path of the electrons becomes longer than the sample-detector distance and the TEY spectrum is independent of the field strength. For higher pressures, the mean free path is too short to allow electron acceleration beyond the ionization threshold of the gas particles. In this regime, ionization events occurring in the gas phase can only be due to dissipation of kinetic energy carried by the electrons emitted from the sample.

**Dr. Carley** opened the discussion of Dr. Flavell's paper: Do you have any direct spectroscopic evidence for the presence of  $\text{Ni}^{3+}$  in your samples? The Ni 2p photoemission spectrum should allow you to identify and quantify the  $\text{Ni}^{2+}:\text{Ni}^{3+}$  ratio.

**Dr. Flavell** responded: In principle, the formal oxidation state for Ni could be determined from the 2p XPS signal. In practice, there is a specific problem for this system in that the strong La 3d<sub>3/2</sub> signal overlaps the Ni 2p<sub>3/2</sub> signal, as noted by Eisaki *et al.*<sup>1</sup> These authors have attempted to deconvolute the signals, but as the Ni signal is rather weak relative to the La signal, detailed analysis of the Ni peakshape for this material is rather difficult.

One might hope that the photon energy of the 3p → 3d resonance might give some indication of oxidation state, but in fact the resonance position for Ni does not shift significantly with oxidation state.<sup>2</sup> (This contrasts with the behaviour of Fe, where the position of the resonance shifts upwards in photon energy quite significantly between Fe<sup>0</sup> and Fe<sup>III</sup>.<sup>3</sup> Here our resonance photon energy is very slightly higher than that in Fe<sup>III</sup>, consistent with results from Mössbauer which show that these materials contain mixed Fe<sup>III</sup> and Fe<sup>IV</sup>.<sup>4</sup>)

The evidence for formal Ni<sup>III</sup> in this system comes mainly from studies of the bulk solid-state chemistry by a combination of titrimetric methods, XRD and Mössbauer (the latter giving information on Fe valencies, and by inference on the Ni<sup>II</sup>/Ni<sup>III</sup> valency once the oxygen excess,  $\delta$ , is determined<sup>4</sup>).

- 1 H. Eisaki, S. Uchida, T. Mizokawa, H. Namatame, A. Fujimori, J. van Elp, P. Kuiper, G. A. Sawatzky, S. Hosoya and H. Katayama-Yoshida, *Phys. Rev. B*, 1992, **45**, 12513.
- 2 M. R. Thuler, R. L. Benbow and Z. Hurych, *Phys. Rev. B*, 1983, **27**, 2082.
- 3 R. J. Lad and V. E. Henrich, *Phys. Rev. B*, 1989, **39**, 13478.
- 4 R. Benloulcif, N. Nguyen, J. M. Grenèche and B. Raveau, *J. Phys. Chem. Solids*, 1991, **52**, 331.

**Prof. Freund** said: My comment refers to the determination of oxidation states from photoelectron spectra. In particular, in the case of Ni 2p spectra of NiO the spectra exhibit intense and complex satellite structures. I would find it difficult to clearly identify the presence of Ni<sup>3+</sup>.

**Dr. Flavell** responded: As you imply, the photoelectron spectra of these highly correlated oxides are complicated by the presence of satellites, in both the valence and core level regions. This does make valence state analysis difficult. However, our understanding of these signals has improved dramatically in the last decade since the discovery of superconducting cuprates, as analogous satellites are observed in the spectra of copper oxides. This has prompted further research into the electronic spectra of related nickelates and cobaltates. Using high quality X-ray photoelectron spectroscopy (XPS) data, and through considering the changes in accessible final states which occur as the formal valence state is changed, it is possible to relate the photoelectron spectra to the formal transition-metal oxidation state.<sup>1</sup>

You will note that I have used the term ‘formal’ oxidation state here, by which I mean the transition-metal oxidation state which results if oxygen is assumed to have a valence state of 2−, and sensible values are assumed for the counteranions. However, in these cuprates and nickelates, there is substantial evidence [*e.g.* from O K-edge X-ray absorption spectroscopy (XAS)<sup>2</sup>] to suggest that the holes introduced by Sr doping have a substantial amount of O character (in this case approximating to O<sup>−</sup>, rather than Ni<sup>3+</sup>). The closeness in energy of O 2p and Ni 3d levels is also reflected in the final states observed in XPS, where the ‘main’ peak of the Ni 2p<sub>3/2</sub> signal is in fact due to creation of the ‘ligand-hole’ final state where an electron is transferred from the oxygen ligand to Ni, and this is at a lower binding energy than the ‘satellite’ peak (in fact from the unscreened 2p<sup>5</sup>3d<sup>8</sup> configuration).

- 1 M. S. Golden, S. J. Golden, R. G. Egdell and W. R. Flavell, *J. Mater. Chem.*, 1991, **1**, 63.
- 2 E. Pellegrin, J. Zaanen, H.-J. Lin, G. Meigs, C. T. Chen, G. H. Ho, H. Eisaki and S. Uchida, *Phys. Rev. B*, 1996, **53**, 10667.

**Prof. Goodman** asked: Have you been able to relate the very nice trends that you have seen in the valence band electronic structure of these materials with their catalytic activity for a particular reaction system?

**Dr. Flavell** responded: In this particular case, the valence band photoemission data gives us three important pieces of information. (1) The states closest to the Fermi energy have both Ni and Fe character. (2) As the system is hole-doped the valence band edge moves towards the Fermi level (as expected), implying that the system becomes more easily oxidisable. Given (1), this implies that it becomes more easy to create  $\text{Ni}^{\text{III}}$  and  $\text{Fe}^{\text{IV}}$ . (3) This movement is larger for systems doped with low levels of Fe than for systems with no Fe.

The last point is particularly interesting because it implies that the system is more easily oxidised with low levels of Fe than without it. The most easily oxidised states will be those filled levels closest to the Fermi energy,  $E_{\text{F}}$  (and in general, the states most readily involved in the catalytic redox cycle will be those close to  $E_{\text{F}}$ ). These have strong Ni character (in addition to Fe character), implying that it becomes more easy to create formal  $\text{Ni}^{\text{III}}$  in the presence of low levels of Fe. We relate this finding to the catalytic activity of the 'real' Hydecatal catalyst. In this system, the activity in hypochlorite decomposition is enhanced by doping the catalyst (based on  $\text{NiO}$ ) with low levels of Fe. The mechanism is thought to involve a rate-limiting  $\text{Ni}^{\text{II}}\text{--Ni}^{\text{III}}$  interconversion,<sup>1</sup> but it is not understood how Fe influences this. Here we show a real effect on the electronic structure of our model material, which suggests that it may indeed be easier to create  $\text{Ni}^{\text{III}}$  in the presence of small amounts of Fe. The redistribution in the filled density-of-states may arise, for example, through strong Ni–O–Fe hybridisation (in turn arising through the closeness in energy of the Fe 3d, Ni 3d and O 2p levels).

So, I would say that in this case we have achieved a rationalisation of the behaviour of the catalytic activity of a particular reaction system. The real challenge lies in using these ideas to predict the behaviour of possible catalyst systems, and we are now developing this approach in collaboration with ICI Katalco.

1 F. King and F. E. Hancock, *Catal. Today*, 1996, **27**, 203.

**Prof. Bowker** said: You have mentioned that the material you are working with is very complicated, but the environment in which the real catalyst works is also a complicated one. It is rather a clever catalyst which is capable of converting sodium hypochlorite into salt and molecular oxygen in aqueous solution. Can you tell us if anything is known about the situation at the surface during this reaction, and what is the active centre for oxygen production?

**Dr. Flavell** responded: A suggested mechanism for operation of the catalyst has recently been published,<sup>1</sup> based on in-house studies at ICI Katalco, and time-resolved EPR measurements at the University of Cardiff.<sup>2</sup> This involves initial activation of the surface by reaction with hypochlorite to form a formal  $\text{Ni}^{\text{IV}}$  species doubly bonded to oxygen, followed (*via* participation of surface  $\text{Ni}^{\text{II}}$ ) by formation of an  $\text{Ni}^{\text{III}}$  dimer bridged by O. The proposal is that this then reacts further with hypochlorite to form a surface peroxy species (bonded to a formal  $\text{Ni}^{\text{III}}$  species).  $\text{O}_2$  is then lost from the surface, returning the surface to its initial state.

1 F. King and F. E. Hancock, *Catal. Today*, 1996, **27**, 203.

2 N. W. Edwards, PhD Thesis, University of Wales, Cardiff, 1993.

**Dr. Davies** opened the discussion of Prof. Thornton's paper: Is there any evidence for oxygen transfer from the zinc surface to the copper islands? Carley *et al.*<sup>1</sup> and Iwasawa *et al.*<sup>2</sup> have shown that the oxidation of CO to  $\text{CO}_2$  and  $\text{CO}_3$  is facile on



copper at low temperatures, therefore the oxygen might be detected by the presence of the characteristic vibrational spectra of these species.

1 A. F. Carley, M. W. Roberts and A. J. Strut, *J. Phys. Chem.*, 1994, **98**, 9175.

2 T. Sueyoshi, T. Sasaki and Y. Iwasawa, *J. Phys. Chem.*, 1996, **100**, 1048.

**Prof. Thornton** responded: The evidence for a Cu metallic character adduced in our earlier work<sup>1,2</sup> suggests that there is little, if any, transfer of O to the Cu islands. Moreover neither CO<sub>2</sub> nor CO<sub>3</sub><sup>2-</sup> species are observed in the near-edge X-ray absorption fine structure (NEXAFS) spectra following CO adsorption. As for IR spectroscopy, we do not see any evidence for CO<sub>2</sub> or carbonate formation following CO exposure to the Cu pre-dosed surface.

1 K. H. Ernst, A. Ludviksson, R. Zhang, J. Yoshihara and C. T. Campbell, *Phys. Rev. B*, 1993, **47**, 13782.

2 C. T. Campbell and A. Ludviksson, *J. Vac. Sci. Technol. A*, 1994, **12**, 1825.

**Prof. Zecchina** asked: Your contribution deals with Co<sup>0</sup> on (000 $\bar{1}$ ) ZnO polar surface. As this surface is polar, (oxygen terminated), we expect that it should be highly unstable and to be consequently heavily reconstructed. Do you have evidence of this? What is known in the more recent literature about this problem?

**Prof. Freund** asked: How well is the structure of the surface known? Specifically, have reconstructions or surface relaxations been identified by recent LEED structure determinations and/or ion scattering data?

**Prof. Thornton** responded to Prof. Zecchina and Prof. Freund: To our knowledge there are four recent studies of the ZnO(000 $\bar{1}$ )-O clean surface crystallography.<sup>1-4</sup> Together the STM<sup>1-3</sup> and XPD<sup>4</sup> studies evidence the presence of a significant concentration of (10 $\bar{1}$ 0) steps, but a relatively small relaxation and rumpling of the (000 $\bar{1}$ ) terraces. The XPD data points to a contraction of 0.2 Å of the top-most oxygen layer.<sup>4</sup> This value (*ca.* 25%) is larger than most values reported for metals<sup>5</sup> although it is comparable with values reported for III-V semiconductors.<sup>6</sup>

1 G. S. Rohrer and D. A. Bonnell, *Surf. Sci.* 1991, **247**, L195.

2 P. M. Thibado, G. S. Rohrer and D. A. Bonnell, *Surf. Sci.*, 1994, **318**, 379.

3 T. M. Parker, N. G. Condon, R. Lindsay, F. M. Leibsle and G. Thornton, in preparation.

4 M. Galeotti, A. Atrei, U. Bardi, G. Rovida, M. Torrini, E. Zanazzi, A. Santucci and A. Klimov, *Chem. Phys. Lett.*, 1994, **222**, 349.

5 J. Sokolov, F. Jona and P. M. Marcus, *Solid State Commun.*, 1984, **49**, 307.

6 C. B. Duke, A. Paton, A. Kahn and D-W. Tu, *J. Vac. Sci. Technol. B*, 1984, **2**, 366.

**Prof. Chesters** said: You make the point that reflection-absorption infrared spectroscopy (RAIRS) on the Zn(000 $\bar{1}$ ) surface is quite insensitive but I wonder whether it should have been possible to detect your proposed carbonate species which are very strong IR absorbers. What, in terms of  $\Delta R\%$ , would you estimate to be the sensitivity limits of RAIRS on the Zn(000 $\bar{1}$ ) surface?

**Prof. Thornton** responded: We can make a semi-quantitative estimate of our RAIRS sensitivity to carbonate by reference to an experiment where we measured formate on the (10 $\bar{1}$ 0) prism face of ZnO.<sup>1</sup> The noise level was *ca.* 0.02% ( $\Delta R/R$ ), and  $\nu_{\text{OCOa}}$ , the strongest absorption band, was 0.1% at a coverage of 0.2 ML.<sup>†</sup> Making a number of rather considerable assumptions, we could say that 0.1 ML of carbonate on ZnO(000 $\bar{1}$ )-O should be at the detection limit. On this basis, our empirical observation that this coverage is below the detection limit is not surprising.

<sup>†</sup> 1 L (langmuir) = 10<sup>-6</sup> Torr s.



- 1 S. Crook, PhD thesis, Manchester University, 1996.

**Dr. Sakakini** asked: What makes the Cu nucleate specifically at the sites which form the carbonate?

Do you really need a Cu coverage of 0.5 ML to annihilate all the step sites on which  $\text{CO}_3^{2-}$  is formed?

**Prof. Thornton** responded: It is quite common for metal overlayer growth to be nucleated at steps,<sup>1–3</sup> which we believe are the bonding sites for carbonate.

In answer to your second question, most probably not, but we do not have the appropriate data for lower coverages.

- 1 T. Jung, R. Schlittler, J. K. Gimzewski and F. J. Himpsel, *Appl. Phys. A*, 1995, **61**, 467.  
 2 J. Jacobsen, L. Pleth Niesel, F. Besenbacher, I. Stensgaard, E. Lægsgaard, T. Rasmussen, K. W. Jacobsen and J. K. Nørskov, *Phys. Rev. Lett.*, 1995, **75**, 489.  
 3 C. T. Campbell, *Surf. Sci. Rep.*, 1997, **227**, 1.

**Prof. Goodman** asked: Have you applied the scanning probe technique to your Cu/ZnO systems particularly the 3D particles/clusters made from the 14 ML Cu film? Also could you comment on the relationship between the IR bands in Fig. 10 of your paper and the abundance of specific Cu facets in the corresponding 3D Cu structures?

**Prof. Thornton** responded: As yet we have not had the opportunity to apply scanning probe methods to Cu overlayers on a ZnO surface, although we hope to carry out such measurements in the near future. As for identifying the concentration of specific facets using the  $\nu_{\text{CO}}$  intensities, dipole coupling effects<sup>1</sup> prevent us from making a meaningful estimate, other than to deduce that there seems to be a higher concentration of (111) and (110) facets than (100).

- 1 P. Hollins, *Surf. Sci. Rep.*, 1992, **16**, 51.

**Dr. Lambert** commented: Your suggestion that step edges on the active sites for carbonate formation from CO is at least consistent with the results of simulations performed by Catlow and co-workers.<sup>1</sup> They showed that the enthalpy for extraction of lattice oxygen by CO is drastically reduced at step edges of oxides. The reaction  $\text{CO(g)} + \text{O(lattice)} \rightarrow \text{CO}_2$  which is endothermic at terrace sites becomes exothermic at edge sites.

- 1 T. X. T. Sayle, S. C. Parker and C. R. A. Catlow, *Surf. Sci.*, 1994, **316**, 329.

**Prof. Stone** asked: The NEXAFS results in Fig. 2 of your paper<sup>1</sup> show that CO adsorption on oxygen-terminated ZnO(000 $\bar{1}$ ) produces two peaks, one ascribed to 'chemisorbed CO' and the other to  $\text{CO}_3^{2-}$ . How do you envisage the former to be bonded, by reaction with a surface  $\text{O}^{2-}$  ion, as in the carbonite ion  $\text{CO}_2^{2-}$  seen spectroscopically on more ionic oxides,<sup>2</sup> or by interaction with a partially extracted  $\text{Zn}^{2+}$  ion?

As regards the formation of  $\text{CO}_3^{2-}$  from CO, 130 K is quite a low temperature to expect full removal of an oxygen from a ZnO step, as depicted in Fig. 7. Is it not possible that the location is such that both of the oxygens used to form  $\text{CO}_3^{2-}$  are still anchored? Is it definite that the desorption at 300 K which diminishes the NEXAFS peaks gives back  $\text{CO}_2$ , or is CO regenerated?

- 1 A. Gutiérrez-Sosa, S. Crook, R. Lindsay, S. Haq, A. Ludviksson, S. Parker, C. T. Campbell and G. Thornton, *Faraday Discuss.*, 1996, **105**, 355.  
 2 M. Bailes, S. Bordiga, F. S. Stone and A. Zecchina, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4675.

**Prof. Thornton** responded: If the CO was bonded to substrate O, the resulting carbonite ion would probably show a difference in the position of the associated NEXAFS resonances. Other studies have also identified CO, as opposed to carbonite, using photoemission. All these studies seem to point to CO adsorbing on a  $\text{Zn}^{2+}$  atom in a  $\text{ZnO}(10\bar{1}0)$  facet exposed at step sites.<sup>1–3</sup> As for the temperature of O abstraction, the relevant diffusion length of O is that appropriate to the selvedge, which we gauge to be substantial even at 130 K. Unfortunately, however, there are no direct experimental data with which to test this hypothesis.

Assuming bonding to  $(10\bar{1}0)$  steps, if both of the O atoms used to form carbonate were still part of the substrate, the plane of the carbonate species would be parallel to the  $(000\bar{1})$  surface, which is inconsistent with the NEXAFS data.

On the final point, we have no TPD data for CO adsorption on the clean  $\text{ZnO}(000\bar{1})$  surface, although we have monitored the TPD from CO adsorbed on the Cu-covered surface.<sup>4</sup>

1 R. R. Gay, M. H. Nodine, V. E. Henrich, H. J. Zeiger and E. I. Solomon, *J. Am. Chem. Soc.*, 1980, **102**, 6752.

2 K. L. D'Amico, M. Trenary, N. D. Shinn, E. I. Solomon and F. R. McFeely, *J. Am. Chem. Soc.*, 1982, **104**, 5102.

3 K. L. D'Amico, F. R. McFeely and E. I. Solomon, *J. Am. Chem. Soc.*, 1983, **105**, 6380.

4 A. Ludviksson, K. H. Ernst, R. Zhang and C. T. Campbell, *J. Catal.*, 1993, **141**, 380.

**Prof. Bowker** commented: Some years ago Ken Waugh and I carried out adsorption–desorption measurements on polycrystalline ZnO powder. We found that adsorption of all the components of the synthesis gas mixture resulted in only weak adsorption with the solid at room temperature, but adsorption at elevated temperature ( $>200^\circ\text{C}$ ) resulted in the formation of a strongly adsorbed state of  $\text{CO}_2$ . Further, adsorption of an  $\text{H}_2$ – $\text{CO}_2$  mix resulted in the formation of an intermediate, the formate species. I would suggest that it would be interesting, in relation to methanol synthesis, if you were to activate the  $\text{CO}_2$  (by gas heating) to form these more strongly bound states which are involved in methanol synthesis.

**Dr. Sakakini** asked: In your paper you have mentioned that annealing the Cu overlayer in which CO has been adsorbed to 400 K, the Cu overlayer transforms or redistributes from 2D islands to 3D islands. Have you checked this transformation?

**Prof. Thornton** responded: Evidence for 2D to 3D island transformation was presented in earlier work.<sup>1,2</sup> XPS results recorded at the time of the present experiments are consistent with this behaviour.

1 K. H. Ernst, A. Ludviksson, R. Zhang, J. Yoshihara and C. T. Campbell, *Phys. Rev. B*, 1993, **47**, 13782.

2 C. T. Campbell and A. Ludviksson, *J. Vac. Sci. Technol. A*, 1994, **12**, 1825.

**Prof. Chesters** asked: You refer to the formation of monolayer epitaxial films of copper on the zinc oxide surface which have (110) orientation and which give '(110)-like' CO infrared spectra. Since a (110) monolayer of copper would consist of well spaced chains of copper atoms, it is difficult to see how such a monolayer on zinc oxide could behave like metallic copper, or why it should adopt the  $\text{Cu}(110)$  unit mesh dimensions. Could you comment on this?

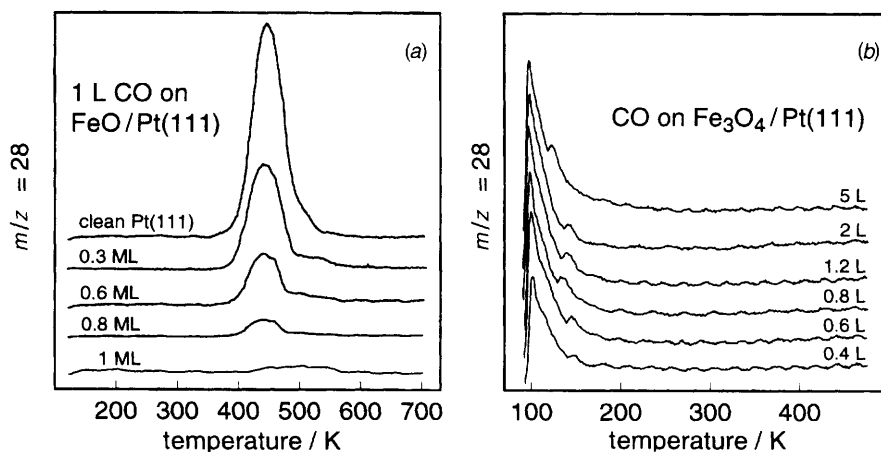
**Prof. Thornton** responded: We describe the copper overlayer as (110)-like on the basis of its physicochemical properties. In particular, the TPD results with probe molecules and the work function are as expected from  $\text{Cu}(110)$ .<sup>1</sup> Moreover, the infrared data presented in the Discussion paper are also consistent with those expected from  $\text{Cu}(110)$ .<sup>2</sup>

- 1 K. H. Ernst, A. Ludviksson, R. Zhang, J. Yoshihara and C. T. Campbell, *Phys. Rev. B*, 1993, **47**, 13782.
- 2 A. Gutiérrez-Sosa, S. Crook, R. Lindsay, G. Thornton, S. Haq, A. Ludviksson, S. Parker and C. T. Campbell, *Faraday Discuss.*, 1996, **105**, 355.

**Dr. Weiss** commented: The authors present interesting NEXAFS and FT-RAIRS measurements on the adsorption of CO and CO<sub>2</sub> onto the ZnO(000 $\bar{1}$ )-O surface. Chemisorbed CO species were observed by NEXAFS at  $T = 130$  K but not with FT-RAIRS, presumably because of the too low sensitivity of the latter technique.

The atomic structure of the ZnO(000 $\bar{1}$ ) surface is still unknown. This polar surface with an outermost hexagonal close-packed oxygen anion layer is expected to be thermodynamically unstable because of its diverging surface potential, which has been calculated *e.g.* by Tasker.<sup>1</sup> In order to stabilize such a surface the surface charge has to be reduced, which can be done in several ways: the formation of surface hydroxyl groups *via* hydrogen adsorption or water dissociation from the residual gas in the chamber as shown *e.g.* for NiO(111) by Freund and co-workers,<sup>2</sup> metal cations located on top of the outermost oxygen layer as found for the Fe<sub>3</sub>O<sub>4</sub>(111) surface by us<sup>3</sup> or the creation of oxygen vacancies in the top oxygen layer.

The chemisorption of CO onto the polar ZnO(000 $\bar{1}$ ) surface with an outermost hexagonal close-packed oxygen anion layer is very unlikely to happen. The zinc cation d-orbitals are very localized in the ionic ZnO crystal and a bonding of the CO molecule to the surface *via* a  $\sigma$ -donor- $\pi$ -acceptor interaction seems not to be possible. For this the molecule has to be very close to the metal cations, which is not possible because the occupied 5s lone pair and 1 $\pi$  molecular orbitals get repelled by the oxygen-terminated surface because of Coulomb interaction and because of the Pauli exclusion principle. We studied the adsorption of CO onto ordered iron oxide films grown onto a Pt(111) substrate with temperature-programmed desorption. Up to one monolayer thickness the film consists of an iron/oxygen bilayer with a hexagonal close-packed oxygen layer on top as shown by photoelectron diffraction (PED) and scanning tunnelling microscopy (STM).<sup>4</sup> The multilayer Fe<sub>3</sub>O<sub>4</sub>(111) film exposes 0.25 monolayer iron cations on top of a hexagonal close-packed oxygen layer. As can be seen in Fig. 1 no CO is adsorbed onto the oxygen-terminated monolayer film completely wetting the platinum surface, whereas CO adsorbed onto the iron-terminated Fe<sub>3</sub>O<sub>4</sub>(111) surface desorbs at a temperature of *ca.* 100 K revealing a desorption energy of 25 kJ mol<sup>-1</sup>, which reflects a very weak



**Fig. 1** Temperature-programmed desorption spectra of CO adsorbed onto an oxygen-terminated FeO(111) monolayer film grown on Pt(111) [lowest curve in (a)] and onto an iron-terminated Fe<sub>3</sub>O<sub>4</sub>(111) film grown on Pt(111) (b). 1 L (langmuir) = 10<sup>-6</sup> Torr s.

chemisorption. Similar adsorption energies have been observed for CO adsorbed onto the non-polar MgO(100) and NiO(100) surfaces, where the carbon atoms are coordinated to surface Ni cations.

Since very few CO molecules are adsorbed onto the ZnO(000 $\bar{1}$ )-O surface, they were not detectable by FT-RAIRS, I suggest that CO is adsorbed at oxygen vacancy sites present on this surface. This could explain the stability of this polar surface and the fact that CO gets adsorbed on this surface. The existence of such oxygen vacancies might be verified by atomic resolution STM images or by a quantitative LEED intensity analysis.

- 1 P. W. Tasker, *J. Phys. C: Solid State Phys.*, 1979, **12**, 4977.
- 2 F. Rohr, K. Wirth, J. Libuda, D. Cappus, M. Bäumer and H.-J. Freund, *Surf. Sci.*, 1994, **315**, L977.
- 3 W. Weiss, A. Barbieri, M. A. VanHove and G. A. Somorjai, *Phys. Rev. Lett.*, 1993, **71**, 1848.
- 4 C. S. Fadley, M. A. VanHove, Z. Hussain and A. P. Kaduwela, *J. Electron Spectrosc.*, 1995, **75**, 273; M. Salmeron, personal communication.

**Prof. Thornton** responded: In a very recent STM study,<sup>1</sup> we observed flat terraces and a high concentration of steps on ZnO(000 $\bar{1}$ )-O. Although we could not achieve atomic resolution from the (000 $\bar{1}$ ) surface, the images of the terraces are sufficiently well defined and flat to suggest that there is not a high concentration of oxygen vacancies. This is not unexpected given that our sample preparation involves annealing in O<sub>2</sub> to restore the stoichiometry. For these reasons we believe that CO reacts with step sites.

- 1 T. M. Parker, N. G. Condon, R. Lindsay, F. M. Leibsle and G. Thornton, in preparation.

**Dr. Davies** opened the discussion of Prof. Waugh's paper: I am not convinced by the assignment of some of the TPD peaks in your paper.<sup>1</sup> The coincident CO<sub>2</sub>-CO-H<sub>2</sub> peaks at 480 K in Fig. 1 for example do suggest the presence of a surface formate but there is no evidence that this is an 'interfacial' species. An alternative assignment would be to formate adsorbed on ZnO(000 $\bar{1}$ ) facets which, as Kung and co-workers have shown<sup>2</sup> decomposes at 480 K to give coincident CO<sub>2</sub>-CO-H<sub>2</sub> peaks.

Also I believe the coincident CO<sub>2</sub> and H<sub>2</sub> peaks at 520–540 K in Fig. 4 and 5<sup>1</sup> are unlikely to be due to a formate species adsorbed on copper. Extensive studies of formic acid and formate on copper surfaces by ourselves<sup>3</sup> and many others, *e.g.* Somorjai<sup>4</sup> and Bowker<sup>5</sup> have not produced any formate species which are stable on copper above 490 K. On the other hand, your own work in 1983<sup>6</sup> showed that pure zinc oxide exposed to a CO<sub>2</sub>-H<sub>2</sub> gas mixture at 530 K gives rise to CO<sub>2</sub> and H<sub>2</sub> adsorption peaks between 510 and 560 K. I suggest that these are likely to be the source of the TPD peaks observed in the present paper.

- 1 B. Sakakini, J. Tabatabaei, K. C. Waugh and F. W. Zemicael, *J. Chem. Soc., Faraday Trans.*, 1996, **105**, 369.
- 2 S. Akhter, K. Lui and H. H. Kung, *J. Phys. Chem.*, 1985, **89**, 1958.
- 3 P. R. Davies and G. G. Mariotti, in preparation.
- 4 G. A. Somorjai and S. S. Fu, *J. Phys. Chem.*, 1992, **96**, 4542.
- 5 M. Bowker, E. Rowbotham, F. M. Leibsle and S. Haq, *Surf. Sci.*, 1996, **349**, 97.
- 6 M. Bowker, H. Houghton, K. C. Waugh, T. Giddings and M. Green, *J. Catal.*, 1983, **84**, 252.

**Prof. Waugh** responded: We assigned the coincident CO<sub>2</sub>-CO-H<sub>2</sub> peaks at 480 K following formic acid adsorption on the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> to some form of interfacial species between the Cu and the ZnO rather than to the oxygen-dominated polar face of ZnO, since in our previous studies on ZnO we had found that formate decomposition from that face resulted in the coincident desorption of CO and H<sub>2</sub> at 570 K with a small amount of CO<sub>2</sub> (*ca.* 1/10th of the amount of CO<sup>1,2</sup>).

In this respect we are clearly at odds with the work of Kung and co-workers to which you refer. In our defence, however, I would state that the polar-face dominated

ZnO used in our study was prepared in an identical fashion to that used in the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst and so it is unlikely that the 480 K CO<sub>2</sub> (dominating) CO–H<sub>2</sub> peaks results from formate decomposition on ZnO.

With respect to your second point, the coincident CO<sub>2</sub>–H<sub>2</sub> peaks at between 520–540 K from the Cu/Al<sub>2</sub>O<sub>3</sub> catalyst must evolve from the Cu component of that catalyst since we have shown in this paper that formate on Al<sub>2</sub>O<sub>3</sub> decomposes to CO and H<sub>2</sub> at *ca.* 560 K. Our work to which you refer<sup>2</sup> for formate decomposition on ZnO, shows that the formate on ZnO desorbs/decomposes as CO and H<sub>2</sub> at 570 K and not to CO<sub>2</sub> and H<sub>2</sub> at 510–560 K as you suggest.

1 M. Bowker, H. Houghton and K. C. Waugh, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 3023.

2 M. Bowker, H. Houghton, K. C. Waugh, T. Giddings and M. Green, *J. Catal.*, 1983, **84**, 252.

**Prof. Joyner** commented: As most people will recognise much of the debate centres on the role, or otherwise of the zinc oxide in this catalyst, when the ‘ICI’ view is that it functions as a true inert support. From your results and the single-crystal studies of Chorkendorff<sup>1</sup> I can construct the following syllogism. (1) You can hydrogenate formate in Cu/ZnO to yield methanol. (2) Chorkendorff cannot hydrogenate formate to yield methanol on copper alone. (3) Therefore, ZnO is necessary to promote methanol synthesis. Would you care to comment?

1 P. A. Taylor, P. B. Rasmussen and I. Chorkendorff, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1267.

**Prof. Waugh** commented: Prof. Joyner’s syllogism reduces to: Chorkendorff and co-workers did not see methanol on hydrogenating a formate species on Cu(100) where no ZnO was present and we did when zinc oxide was present.

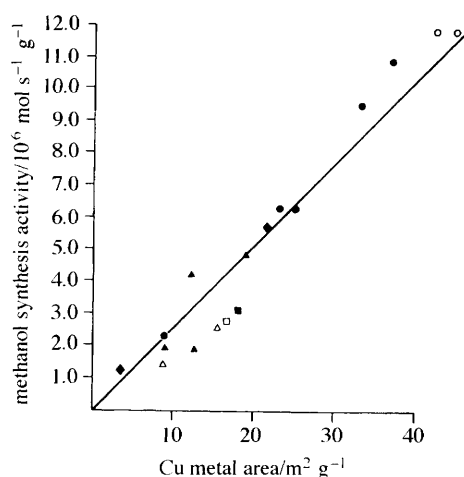
The conclusion therefore is that Cu alone is insufficient and ZnO in combination with Cu is a pre-requisite for methanol synthesis activity. There are many reasons which can be cited to show that this logic is false. First, our observation of a linear relationship between copper metal area and methanol synthesis activity for copper in combination with MnO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> as well as with ZnO and the industrial ZnO/Al<sub>2</sub>O<sub>3</sub> shows the Cu/ZnO combination to be neither unique nor essential. The turnover number (the number of molecules produced per copper site per second) is the same for each of these catalysts<sup>1</sup> (see Fig. 1). Additionally, although we have not published it because the point was so close to the origin, under the same conditions to those cited above,<sup>1</sup> turnover number for copper metal alone was the same as for the oxide-supported copper catalysts.

Secondly, the desorption/decomposition peak maximum for formate adsorbed on copper is the same as that from the copper/zinc oxide combination.<sup>2</sup> The zinc oxide therefore does not effect the stability of the pivotal intermediate in the reaction, hydrogenation of which is believed to be the rate-determining step in the reaction.<sup>2</sup> The conclusion was taken that no synergy attaches to the Cu/ZnO combination in terms of the detailed kinetics of the reaction.

The reason that Chorkendorff and co-workers were unable to detect any methanol when they attempted to hydrogenate the formate adsorbed on Cu(100) and we could on a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is a simple one of sensitivity. We had a copper metal area *ca.* 10<sup>5</sup> times that of Chorkendorff and were able to measure 2.05 × 10<sup>19</sup> molecules of methanol on hydrogenation of the formate. For a similar coverage of formate they would be attempting to detect 2 × 10<sup>14</sup> molecules of methanol. This would have been well below our detection limit.

1 G. C. Chinchin, K. C. Waugh and D. A. Whan, *Appl. Catal.*, 1986, **25**, 101.

2 M. Bowker, R. A. Hadden, H. Houghton, J. N. K. Hyland and K. C. Waugh, *J. Catal.*, 1988, **109**, 263.



**Fig. 1** Methanol synthesis activity as a function of copper-metal area; (●) CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> (60 : 30 : 10), (◆) CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> (45 : 37 : 18), (○) CuO/SiO<sub>2</sub>, (▲) CuO/Al<sub>2</sub>O<sub>3</sub>, (△) CuO/MgO, (□) CuO/MnO, (■) CuO/ZnO

**Prof. Bowker** commented: First, in response to Prof. Joyner's comment relating to the work of Chorkendorff *et al.* I believe what they observed was that formate was lost from the surface, but they did not identify methanol as a product. However, I also believe they did not directly identify what happened to the lost formate. It is possible that hydrogenation of formate to formic acid occurs; this may well be a facile reaction and since formic acid is such a 'sticky' molecule it may be adsorbed on the walls of the reactor and may not reach the detector.

Secondly, regarding the identification of formate presence on Cu using a TPD peak temperature; we have recently been examining formate stability on both highly oxidised Cu single crystals [*e.g.*  $c(6 \times 2)$  structure] and on copper(I) and (II) oxide surfaces. From this, formate on copper oxides can have a wide range of TPD temperatures, ranging from near room temperature to the highest temperature state of formate on clean copper at 450 K.

**Prof. Waugh** communicated: Prof. Bowker's suggestion that Chorkendorff and co-workers' inability to observe methanol upon hydrogenation of the adsorbed formate on Cu(100) was because it formed formic acid which, once desorbed, adsorbed strongly on the walls of the chamber and therefore was not observed. While initially appealing, further consideration shows that it cannot be the case. The work we have presented here shows, by virtue of the carbon balance which exists between the formate species adsorbed on the copper and the methanol produced by hydrogenation of that formate, that the ineluctable fate of the formate upon hydrogenation is to produce methanol. Formic acid cannot be an intermediate product in the sequence of formate to methanol since this would require the formic acid to be formed, desorb and then re-adsorb into some new type of formate which inevitably would form methanol and not formic acid. This violates the principle of microscopic reversibility.

If it were argued that hydrogenation of the formate adsorbed on the copper could have two reaction pathways, formic acid and methanol, then by readsorption and further reaction of both formic acid and methanol necessarily both products would always be observed. Our work has shown that methanol is the inescapable fate of the



hydrogenation of formate and so formic acid cannot be formed as some intermediate product or as a by-product.

**Prof. Bowker** communicated: This last statement is incorrect. Several authors carrying out TPD on formate adsorbed on copper have reported formic acid production during formate decomposition *i.e.* self-hydrogenation.<sup>1,2</sup> This is rate-limited by the formate decomposition and is therefore relatively facile.

Further, I don't propose gas-phase formic acid as an intermediate in methanol synthesis. Its most likely fate is to decompose with high efficiency back to reactants ( $\text{CO}_2$  and  $\text{H}_2$ ) under the high temperature of methanol synthesis. Thus, under those conditions (which are quite different from Chorkendorff's) very little formic acid would be seen at the exit of reactor.

1 F. Henn, J. Rodriguez and C. T. Campbell, *Surf. Sci.*, 1990, **236**, 282.

2 M. Bowker, E. Rowbotham, F. Leibsle and S. Haq, *Surf. Sci.*, 1996, **349**, 97.

**Prof. Somorjai** asked: Can the role of ZnO be to produce certain copper crystal faces that are optional for the hydrogenation of the formate?

**Prof. Waugh** responded: It is entirely possible that the role of the zinc oxide is to produce an optimal surface population of given copper crystal faces. Our observation here for a new more stable formate species on the copper component of a  $\text{Cu}/\text{Al}_2\text{O}_3$  catalyst which decomposes to  $\text{CO}_2$  and  $\text{H}_2$  at 545 K is entirely consistent with this suggestion. However, our observation that  $\text{Cu}/\text{SiO}_2$  was more active than any  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst<sup>1</sup> suggests that while stepped surfaces are probably instrumental in the initial stages of methanol syntheses ( $\text{CO}_2$  decomposition and subsequent  $\text{CO}_3^{2-}$  formation), the formate once formed is mobile and can be hydrogenated on any crystal face.

1 G. C. Chinchén, K. C. Waugh and D. A. Whan, *Appl. Catal.*, 1986, **25**, 101.

**Prof. Spencer** commented: As the copper crystallites in industrial  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalysts are some 50 Å in size, it is *a priori* difficult to see how any  $\text{Cu}/\text{ZnO}$  interfacial efforts could be of significance in methanol synthesis. However, there is a possible mechanism by which this could happen. The conditions under typical catalyst reduction can give rise to  $\alpha$ -brass formation in surface layers of the copper crystallites.<sup>1</sup> Reaction mixtures are more oxidising and lead to oxidation of any surface brass, giving copper metal and a decoration of zinc oxide.

Do Prof. Waugh's results give any indication whether the formate intermediate is made directly from  $\text{CO}_2$  and hydrogen or indirectly *via* a surface carbonate?

1 M. S. Spencer, *Surf. Sci.*, 1987, **192**, 323; 329; 336.

**Prof. Waugh** responded: The suggestion that, under normal industrial reaction conditions using a  $\text{CO}-\text{CO}_2-\text{H}_2$  feed, the surface of the copper metal is decorated with ZnO is an intriguing one. Nevertheless, since  $\text{Cu}/\text{SiO}_2$  is more active than  $\text{Cu}/\text{ZnO}$  and since the activity simply scales with copper metal area this ZnO decorated copper is not intrinsically more active than copper itself.

In respect of the second point, the work presented here cannot shed any light on whether formate is made from adsorbed  $\text{CO}_2$  or an adsorbed carbonate. Previously,<sup>1</sup> however, using temperature-programmed reaction in which the surface species on a  $\text{SiO}_2$ -supported copper catalyst were monitored, *in situ*, using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), we found that a symmetric carbonate was formed at low temperatures, (*ca.* 300 K), it being quantitatively transformed to formate on raising the temperature to *ca.* 400 K. Formate is therefore formed by hydrogenation of the carbonate adsorbed on the copper.

1 G. J. Millar, C. H. Rochester and K. C. Waugh, *Mol. Phys.*, 1991, **76**, 833.

**Prof. Stone** commented: Regarding the role of ZnO in the Cu/ZnO methanol synthesis catalyst, it is important to consider not only the formation of the formate, but also the second stage, its hydrogenation to methanol. I prefer the view that the role of ZnO is mainly to facilitate the hydrogenation of the formate which has been formed on the copper, a reaction which can occur very effectively at the interface between the two phases, using the reservoir of  $H_{ads}$  available at synthesis temperature on the zinc oxide.

**Prof. Waugh** responded: Prof. Stone's preferred view that the role of the zinc oxide is to act as a reservoir of  $H_{ads}$  and thereby to facilitate hydrogenation of the formate at the copper/zinc oxide interface is an appealing one. However, here again, our observation of a linear relationship between methanol synthesis activity and copper metal area, a relationship which holds for copper in combination with oxides other than zinc oxide *e.g.* manganese oxide, alumina and silica with the latter providing the most active catalyst,<sup>1</sup> suggests that should zinc oxide be a provider of  $H_{ads}$  to the copper, it is of little overall consequence to the activity of the copper in methanol synthesis.

1 G. C. Chinchin, K. C. Waugh and D. A. Whan, *Appl. Catal.*, 1986, **25**, 101.

**Prof. Spencer** communicated: Prof. Somorjai has raised the controversial question of the role of ZnO in the copper-based methanol synthesis catalysts. Prof. Stone has suggested that hydrogen chemisorption on ZnO could be a significant part of the process. As Prof. Waugh has indicated, there have been many conflicting experimental results in this area. Work by the ICI group<sup>1</sup> gave a linear relation between copper metal surface area and rate of methanol synthesis, *i.e.* constant specific activity, for a range of catalysts. This needs some qualification, for in a later and more accurate study<sup>2</sup> by the ICI group than that shown here by Prof. Waugh, the deviations from constant specific activity were found to be greater than experimental error. Thus, there is at least some second-order effect on activity, confirmed by Fujitani *et al.*<sup>3</sup>

In contrast, several other groups<sup>4</sup> observed a strong dependence of activity on support oxide, with ZnO showing a prominent positive synergy. Burch and Spencer<sup>4</sup> interpreted these results in terms of hydrogen spillover between Cu and ZnO phases, confirmed by NMR studies.<sup>5</sup>

Some of these diverse observations can be understood in terms of the different catalyst test conditions used by different groups. The ICI group<sup>1,2</sup> used tests corresponding to the inlet of an industrial reactor [very low conversions, total pressure of 50–100 bar, high  $H_2/(CO + CO_2)$  ratio]. It is probable that this gives an ample supply of adsorbed H [ $H(a)$ ] on the Cu surface directly from  $H_2$  chemisorption, with synthesis rate then controlled largely by formate hydrogenolysis. Other groups<sup>4</sup> used higher conversions, lower pressures and stoichiometric  $H_2/(CO + CO_2)$  ratios. With high coverages of the Cu surface by reaction intermediates,  $H_2$  chemisorption could then become rate limiting on, *e.g.*, a Cu/SiO<sub>2</sub> catalyst, so resulting in lower catalyst activity. In this system synergy by ZnO can be understood:  $H_2$  chemisorption on ZnO, followed by  $H(a)$  spillover on to the Cu surface, could supplement the supply of  $H(a)$  on the Cu surface and return the rate-limiting step to formate hydrogenolysis. In all these cases the catalyst activity would be expected to be proportional to copper metal area for a given type of catalyst and given test conditions. It follows from this analysis that although a synergy effect by ZnO is not relevant at the inlet of an industrial reactor, this may be so towards the reactor exit.

1 G. C. Chinchin, K. C. Waugh and D. A. Whan, *Appl. Catal.*, 1986, **25**, 101.

2 G. C. Chinchin and M. S. Spencer, *Catal. Today*, 1991, **10**, 293.

3 T. Fujitani, M. Saito, Y. Kanai, T. Kakumoto, T. Watanabe, J. Onakemura and T. Uchijima, *Catal. Lett.*, 1994, **25**, 271.

4 R. Burch, S. E. Golunski and M. S. Spencer, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 2683.

5 P. R. Dennison, K. J. Packer and M. S. Spencer, *J. Chem. Soc., Faraday Trans.*, 1989, **85**, 3537.

**Prof. Waugh** communicated in response: Prof. Spencer's claim that a second study of methanol synthesis rates as a function of copper metal area<sup>1</sup> was more accurate than the first<sup>2</sup> is difficult to substantiate since the method and equipment employed were the same in both studies. All that can be said of the data presented in the later paper is that there is a greater scatter on the activity–area plot than in the earlier one. Whether this is significant and can be ascribed to some second-order effect is debatable.

1 G. C. Chinchin and M. S. Spencer, *Catal. Today*, 1991, **10**, 293.

2 G. C. Chinchin, K. C. Waugh and D. A. When, *Appl. Catal.*, 1986, **28**, 101.

**Prof. Bowker** commented: There has been much discussion over the last 15 years or so regarding the details of the mechanism of methanol synthesis, and in particular, of the role of ZnO. The current view seems to be that ZnO is only useful as a specific support to enable the correct copper configuration, or as a sink for poisons such as S. Linear correlations of methanol synthesis activity with copper metal used for several supported catalysts seem to support the view that copper is the significant active phase and the support has no role other than maintaining copper area. However, it seems too much of a coincidence that ZnO was the preferred catalyst prior to lower pressure/temperature Cu catalysts. It may be that there is an active role for ZnO, but that the steps it facilitates do not include the rate-determining step. Perhaps the oxidic support is the centre for adsorption of CO<sub>2</sub>, or maybe even of H<sub>2</sub>, both of which are highly activated on copper. Support for an active role for Zn comes from Fujitani and co-workers<sup>1</sup> who have published several papers recently on this subject. They claim that Cu<sup>+</sup> is the important species required for high activity synthesis, and that the linear dependence of activity upon copper metal area does not hold for all copper catalyst.

It may be that the rate-determining step is one occurring on the copper component and involves formate breakdown, probably the breaking of the C–O bond in that intermediate. Nevertheless, the support may be involved in steps leading to the production of the formate species.

1 J. Nakamura, T. Uchijima, Y. Kanai and T. Fujitani, *Catal. Today*, 1996, **28**, 223.

**Prof. Waugh** responded: I believe the figure shown in response to Prof. Joyner's question which shows a linear relationship between copper metal area and methanol synthesis activity in which copper is combined with oxides other than ZnO *e.g.* MnO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> is quite unequivocal. Copper is equally active regardless of the presence or absence of ZnO.

**Prof. Goodman** asked: Regarding the need for the ZnO support in hydrogen dissociation, have you or anyone for that matter convoluted a Battyman distribution at your reaction temperatures or pressures onto the relevant molecular beam data to estimate the absolute rate at which hydrogen dissociates on copper? That is, does hydrogen dissociate faster than necessary to turnover CH<sub>3</sub>OH at the observed rate found in your experiment?

**Prof. Waugh** responded: The rate of hydrogen adsorption far exceeds that of methanol synthesis. For an activation energy of adsorption of 11 kcal mol<sup>−1</sup> for hydrogen adsorption on Cu, the sticking probability of hydrogen is *ca.*  $2 \times 10^{-5}$  at 500 K. At 50 bar and 80% hydrogen for which the methanol synthesis rate was measured in Fig. 1 in our paper, the rate of hydrogen adsorption is  $8 \times 10^5$  monolayer s<sup>−1</sup> or  $8 \times 10^{-5}$  molecule site<sup>−1</sup> s<sup>−1</sup>. The methanol synthesis rate calculated from the figure is  $10^{-2}$  molecule

site<sup>-1</sup> s<sup>-1</sup> and so it is clear that the rate of adsorption of hydrogen on Cu far exceeds the rate of methanol synthesis on that metal.

**Prof. Somorjai** asked: Is there a possibility that the formate is hydrogenated to formic acid? Is there any evidence of formic acid formation perhaps in the liquid phase?

**Prof. Waugh** responded: The carbon balance we have demonstrated in this paper between the methanol produced and the formate deposited on the surface shows that, for some as yet unclear reason, the formate is hydrogenated with 100% selectivity to methanol. Formic acid is not formed by the hydrogenation of a formate species adsorbed on copper.

**Dr. Davies** commented: Prof. Bowker has suggested that since CO<sub>2</sub> does not readily chemisorb on copper the role of ZnO in the low-temperature methanol synthesis catalyst is to supply CO<sub>2</sub>. Our results presented earlier in this Discussion however,<sup>1</sup> show that in the presence of low concentrations of surface oxygen, CO<sub>2</sub> reacts readily with copper surfaces to form a carbonate. In the working catalyst the copper surface is unlikely to be fully reduced and therefore since Prof. Waugh has shown<sup>2</sup> that at copper surfaces carbonate is readily hydrogenated to formate and the latter to methanol it is clear that the whole CO<sub>2</sub> to CH<sub>3</sub>OH pathway can take place on the copper surface alone.

1 A. F. Carley, A. Chambers, P. R. Davies, G. G. Mariotti, R. Kurian and M. W. Roberts, *Faraday Discuss.*, 1996, **105**, 225.

2 G. J. Millar, C. H. Rochester and K. C. Waugh, *Mol. Phys.*, 1991, **76**, 833.

**Prof. Waugh** responded: It is obvious that I agree entirely with Dr. Davies' comment that copper alone is the active component. Our suggestion that the role of ZnO was to act as provider of CO<sub>2</sub> to the copper was put forward to try to account in some way for the apparent synergy of Cu and ZnO in methanol synthesis.<sup>1</sup> The linear relationship shown in the figure caused us to discard any mechanistic role for the ZnO.

1 G. C. Chinchin, K. C. Waugh and D. A. Whan, *Appl. Catal.*, 1986, **25**, 101.

**Prof. Joyner** said: I would like to issue a challenge to those who say that zinc oxide is an inert support in methanol synthesis, based on the observation that good copper catalysts can also be made with other partially reducible oxides such as ceria and thoria.

Can you make a copper catalyst on a truly inert support (SiO<sub>2</sub>, carbon, possibly even Al<sub>2</sub>O<sub>3</sub>) which will give a stable space time yield as good, or better than, Cu/ZnO?

**Prof. Waugh** responded: Reference to the figure in response to your first question (p. 396) shows that it has already been done.