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Comments

Comment on "Comments on controlling reaction selectivity in the oxidation of methanol at Cu(110) surfaces"

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In a comment on our recent paper [1] in Catalysis Letters, Bowker et al. confirm [2] our observation that the coadsorption of methanol and dioxygen at a Cu(110) surface opens up a much more facile pathway to formate than is available through sequential adsorption at room temperature. They also agree with our proposal that the facile kinetics in this case arise from the availability of more reactive oxygen states in the coadsorption experiment; a model advanced several years ago by Roberts and co-workers in connection with ammonia/dioxygen coadsorption on magnesium [3,4], zinc [5] and copper [6,7] surfaces.

Despite its general agreement with our work there are a number of aspects of the paper from Bowker et al. on which we would like to comment. In particular we would like to explore their statement that "*little or no formate is produced on Cu(110) by sequential dosing of oxygen and methanol*". The critical point about this statement is that it ignores the effect of temperature on the results of the experiment. In fact when one reviews the literature one finds that Bowker and co-worker's frequent assertion that formate is not formed from methanol oxidation on copper surfaces is based entirely on experiments that involve methanol adsorption at low temperatures, primarily those of Madix and Bowker in 1980 [8] and Leibsle et al. in 1994 [9]. In these experiments methanol was adsorbed at preoxidised Cu(110) surfaces at 140 and 260 K respectively. In the former case "*no evidence for the presence of formate was found*" whereas in the latter, evidence for formate from CO_2 desorption was observed but the authors noted that "*the CO_2 peak ... were small compared with that evolved from formate decomposition after formic acid adsorption*". The authors of the comment [2] make much of the fact that the small yield of formate (based on CO_2 desorption) agrees well with the results of Fu and Somorjai [10] and of Russell and co-workers [11] but the latter experiments also involved methanol adsorption at low temperatures.

We have shown [12,13] that the temperature at which methanol is adsorbed at copper surfaces is an important parameter in TPD experiments, adsorption at low temperatures giving rise to negligible amounts of formate, as previously reported [8], but adsorption at room temperature, and above, giving significant formate yields. This is entirely in line with an XPS study [14] which showed that whilst adsorbed methoxy species are stable on Cu(110)/O(a) at 260 K, they react readily to give formate at higher temperatures (350 K). Interestingly, earlier work [15] involving one of the authors of the comment [2] showed substantial yields of formate following methanol adsorption at **room temperature** on a "partially oxidised" copper catalyst. Nevertheless, even in 1996 Bowker et al. still [16] cite experiments involving low-temperature methanol adsorption to support their claim that "*oxygen (2 × 1) precovered Cu(110) surfaces ... have negligible activity toward formate production when subsequently dosed with methanol*".

The neglect of temperature as an experimental parameter has serious consequences for the interpretation of much of the data published in recent years on methanol oxidation. For example in a TPD study on a copper/palladium bimetallic surface, Newton and Bowker reported [17] formate formation after methanol adsorption at **room temperature**. They concluded that since the formate route "*does not occur to any appreciable degree under the same conditions for Cu(110)*" (our underlining) there must be a "*modification of adsorbate stability ... due to a ligand effect arising from the presence of palladium in the second layer*". To reach this conclusion, however, the authors compared their results to the TPD experiments of Madix and Bowker [8] in which, as mentioned above, methanol was adsorbed at **140 K**. When one compares the results on the bimetallic surface with experiments [12,13] on copper under **precisely** the same conditions (i.e. methanol adsorption at room temperature) one finds that the presence of the palladium causes **no** significant change in the reaction pathway.

Another example where the temperature sensitivity of the methanol oxidation pathway to formate may be of crucial significance is in the interpretation of molecular beam experiments [9,18]. The model used in these papers entirely neglects the possibility of the oxidation of methoxy to formate. This assumption would probably be justified for temperatures of 260 K and below but will cause serious error when the sample temperature is 300 K or greater. Interestingly, the molecular beam results show a change of mechanism between 423 and 450 K where, as is well known, the rate of formate decomposition becomes significant.

Bowker et al. have criticised our statement "*the accepted mechanism for methanol oxidation at copper surfaces . . . has only recently been updated to include oxidation to formate*". We note that the articles from the Reading group in 1996 [2,19] are the first papers by them since 1980 to include the oxidation of methoxy to formate in a suggested mechanism. Presumably the authors would agree that at the time their previous papers [9,18,20,21] were published their mechanism was the "accepted mechanism" and we therefore stand by our original comment.

A third issue raised by Bowker et al. is the identification of adsorbed formate on the copper surface after the coadsorption experiment. They claim [2] "*our STM data do demonstrate that formate production occurs at 300 K*". This is misleading; STM may identify a c(2×2) structure at the copper surface but this could be due to surface species other than formate. Interestingly, earlier STM-based papers [9,21] from the same group reported "methoxy derived" c(2×2) structures under conditions where they contend [2] "*that little or no formate is produced*". One must conclude either that formate is indeed produced in their sequential adsorption experiments or else, that STM images cannot reliably identify surface intermediates in this system. Fortunately, using XPS [22], which is a direct chemical probe, we have established unequivocally the presence of significant concentrations of formate on the Cu(110) surface after the coadsorption of methanol and dioxygen at room temperature.

Finally, we note that during the last decade Roberts and co-workers have exploited the "co-adsorption" approach to surface chemistry in a large number of different systems [3–7,13,23–30] leading to the identification of new reaction pathways and new insights into catalytic mechanisms. One of the central concepts of this work has been the unique reactivity associated with each of several different states of oxygen at metal surfaces, including molecular [5], hot [6,25,31], isolated [7,28,30] and islanded [7,28] oxygen atoms. It has also demonstrated [24,26,29,32] the way in which different reaction conditions including preadsorption, coadsorption and adsorption at different temperatures can be used to control the relative surface concentrations of different oxygen states and thus select different reaction pathways. These ideas are now being taken on board by groups elsewhere [33–35] and have presumably provided the impetus for the recent work of Bowker et al. [2,16].

Note added in proof

We are grateful to Dr. Leibsle for sending us a copy of his recent article, before publication, in which he also notes [36] the discrepancy between the conclusions of Bowker et al.'s recent papers [2,16] and previous work [9] in the literature.

References

[1] P.R. Davies and G.G. Mariotti, Catal. Lett. 43 (1997) 261.

[2] M. Bowker, S. Poulston, R.A. Bennett and A.H. Jones, Catal. Lett. 43 (1997) 267.

[3] C.T. Au and M.W. Roberts, Nature 319 (1986) 206.

[4] C.T. Au and M.W. Roberts, J. Chem. Soc. Faraday Trans. I 83 (1987) 2047.

[5] A.F. Carley, S. Yan and M.W. Roberts, J. Chem. Soc. Faraday Trans. 86 (1990) 2701.

[6] B. Afsin, P.R. Davies, A. Pashusky, M.W. Roberts and D. Vincent, Surf. Sci. 284 (1993) 109.

[7] A.F. Carley, P.R. Davies, M.W. Roberts and D. Vincent, Topics Catal. 1 (1994) 35.

[8] R.J. Madix and M. Bowker, Surf. Sci. 95 (1980) 190.

[9] S.M. Francis, F.M. Leibsle, S. Haq, N. Xiang and M. Bowker, Surf. Sci. 315 (1994) 284.

[10] S.S. Fu and G.A. Somorjai, J. Phys. Chem. 96 (1992) 4542.

[11] J.N. Russell, S.M. Gates and J.T. Yates, Surf. Sci. 163 (1985) 516.

[12] A.F. Carley, P.R. Davies, G.G. Mariotti and S. Read, Surf. Sci. 364 (1996) L525.

[13] P.R. Davies and G.G. Mariotti, J. Phys. Chem. 100 (1996) 19975.

[14] A.F. Carley, A.W. Owens, M.K. Rajumon, M.W. Roberts and S.D. Jackson, Catal. Lett. 37 (1996) 79.

[15] M. Bowker, R.A. Hadden, H. Houghton, J.N.K. Hyland and K.C. Waugh, J. Catal. 109 (1988) 263.

[16] S. Poulston, A.H. Jones, R.A. Bennett and M. Bowker, J. Phys. Conden. Matter 8 (1996) L765.

[17] M.A. Newton and M. Bowker, Catal. Lett. 21 (1993) 139.

[18] C. Barnes, P. Pudney, Q.M. Guo and M. Bowker, J. Chem. Soc. Faraday Trans. 86 (1990) 2693.

[19] M. Bowker, Topics Catal. 3 (1996) 461.

[20] F.M. Leibsle, S.M. Francis, R. Davis, N. Xiang, S. Haq and M. Bowker, Phys. Rev. Lett. 72 (1994) 2569.

[21] F.M. Leibsle, S.M. Francis, S. Haq and M. Bowker, Surf. Sci. 318 (1994) 46.

[22] A.F. Carley, A. Chambers, P.R. Davies, G.G. Mariotti, R. Kurian and M.W. Roberts, Faraday Disc. (1997).

[23] M.W. Roberts, Chem. Soc. Rev. 18 (1989) 451.

[24] M.W. Roberts, Appl. Surf. Sci. 52 (1991) 133.

[25] B. Afsin, P.R. Davies, A. Pashuski and M.W. Roberts, Surf. Sci. 259 (1991) L724.

[26] M.W. Roberts, J. Mol. Catal. 74 (1992) 11.

[27] P.R. Davies and M.W. Roberts, J. Chem. Soc. Faraday Trans. 88 (1992) 361.

[28] A.F. Carley, P.R. Davies, M.W. Roberts, N. Shukla, Y. Song and K.K. Thomas, Appl. Surf. Sci. 81 (1994) 265.

[29] M.W. Roberts, Surf. Sci. 300 (1994) 769.

[30] P.R. Davies, M.W. Roberts, N. Shukla and D.J. Vincent, Surf. Sci. 325 (1995) 50.

[31] A.F. Carley and M.W. Roberts, J. Chem. Soc. Chem. Commun. (1987) 355.
[32] M.W. Roberts, Catal. Today 12 (1992) 501.
[33] X.C. Guo and R.J. Madix, Surf. Sci. 367 (1996) L95.
[34] C.J. Hirschmugl, K.M. Schindler, O. Schaff, V. Fernandez, A. Theobald, P. Hofmann, A.M. Bradshaw, R. Davis, N.A. Booth, D.P. Woodruff and V. Fritzsche, Surf. Sci. 352 (1996) 232.
[35] J. Buisset, H.P. Rust, E.K. Schweizer, L. Cramer and A.M. Bradshaw, Surf. Sci. 349 (1996) L147.
[36] F. Leibsle, private communication, J. Phys. Condens. Matter, accepted.