Contrasting reaction pathways in methanol oxidation on Cu(110) studied by STM

LETTER TO THE EDITOR

Contrasting reaction pathways in methanol oxidation on Cu(110) studied by STM

S Poulston, A H Jones†, R A Bennett and M Bowker

Reading Catalysis Research Centre, Chemistry Department, University of Reading, Whiteknights Park, Reading RG6 6AD, UK
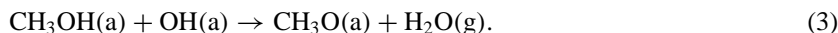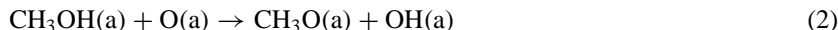
Abstract. Scanning tunnelling microscopy (STM) has been employed in studying the adsorption and reaction of methanol and oxygen on Cu(110) during co-dosing. We have observed the production of formate $c(2 \times 2)$ and (3×1) structures at 300 K during co-dosing. This strongly contrasts with the established case of sequential dosing, since oxygen (2×1) precovered Cu(110) surfaces are seen to have negligible activity toward formate production when subsequently dosed with methanol. During co-dosing formate and methoxy groups are seen as the main reaction products while oxygen (2×1) reconstructed areas poison the formate production channel. Competition for isolated oxygen adatoms between the O (2×1) islands and methoxy groups is seen as determining the rate of formate production. Methanol rich gas mixtures have the highest efficiency for formate production whereas an oxygen rich gas phase composition does not produce formate due to preferential growth of O (2×1) islands.

Most surface science studies involving the reaction of two or more adsorbates have predominantly focused on the interaction of reactants dosed sequentially. However there is a growing sentiment that such an approach is limited and that co-dosing by the simultaneous introduction of reactants may lead both to alternative reaction pathways and to a more realistic model of catalytic activity. We have employed STM and the co-dosing methodology on the methanol–oxygen/Cu(110) system and contrast these new results with the well established reactivity occurring when Cu is exposed sequentially to oxygen and then methanol.

The adsorption, reaction and decomposition of methanol (MeOH) and oxygen on copper surfaces has become a model system for the understanding of chemical catalysis [1–9]. On both clean and oxygen precovered (110) surfaces these processes have been investigated by many techniques [1–4]. Of particular interest on the oxygen reconstructed surface has been the precursor mediated reaction to produce adsorbed methoxy (methanol with the alcohol hydrogen removed) [5]. In this model the incident methanol molecule is trapped in a short-lived physisorbed state and is free to rapidly diffuse across the surface to 'search for' an active site for reaction. Recent scanning tunnelling microscopy (STM) studies [6, 7] have shown that this methanol precursor molecule preferentially attacks terminal atoms of the oxygen (2×1) reconstruction, the reaction front propagating along the rows leaving adsorbed methoxy phase separated from the oxygen, and liberating water ((1)–(3)). The notion that terminal atoms are of higher reactivity than atoms associated with either the

---

† Now at Oxford Instruments, Scientific Research Division (Cambridge), SPM Group, Chesterton Mills, French's Road, Cambridge CB4 3NP, UK.

sides or the centre of the (2×1) oxygen islands is interesting in that it identifies the 'Holy Grail' of catalysis, namely the active site.

$$CH_3OH(g) \rightarrow CH_3OH(a) \tag{1}$$

$$CH_3OH(a) + O(a) \rightarrow CH_3O(a) + OH(a) \tag{2}$$

$$CH_3OH(a) + OH(a) \rightarrow CH_3O(a) + H_2O(g). \tag{3}$$

Sequential adsorption, at room temperature, of oxygen followed by methanol leads exclusively to the formation of adsorbed methoxy [8] and, depending upon oxygen precoverage, residual oxygen islands. For an oxygen saturated surface methoxy formation is inhibited as the stoichiometry at room temperature dictates that two methanol molecules are required to remove one oxygen atom [6], ((1)–(3)). The surface density of adsorbed methoxy is lower than that of the oxygen and thus the reaction cannot proceed due to lack of clean surface for large oxygen precoverages. These phase separated species are not seen to react in STM at room temperature; however production of formate has been reported *during* temperature programmed desorption (TPD) [9]. A reaction mechanism in which oxygen (2×1) islands evaporate reactive adatoms onto the clean surface has previously been proposed to account for the increased reactivity of oxygen (2×1) at elevated temperatures in the oxidation of CO to CO_2 [10]. A similar mechanism could account for the observed formate production during TPD. In further support of the isolated oxygen adatoms invoked as the active species in this model Sueyoshi *et al* [11, 12] have undertaken experiments in which CO and O_2 were co-dosed, producing significantly higher reaction rates than would be expected for sequential adsorption even at low temperature. Furthermore Afsin *et al* have observed the operation of different reaction pathways for co-dosing and sequential dosing of NH_3 and O_2 on Cu(110) [13]. This STM study concentrates on the role of isolated oxygen atoms produced by co-dosing of oxygen and methanol on Cu(110) in the conversion of methoxy to formate and invokes an alternative reaction pathway in this system which is not observed during sequential dosing.

The variable-temperature STM and UHV chamber employed in this study was produced commercially by WA Technology (now Oxford Instruments) and is described in detail elsewhere [14]. The Cu(110) sample was cleaned using cycles of Ar^+ ion bombardment (500 eV, 10 μA) at 720 K, cooling to room temperature in the ion beam and vacuum annealing to 720 K. This procedure produced a good (1×1) LEED pattern and left no detectable trace of sulphur or carbon in AES.

All experiments were carried out on the clean Cu(110) surface at room temperature ($\sim$300 K). For co-dosing the two gases were mixed in the gas line and dosed through a single leak valve. A VG Quadrupole mass spectrometer was used to compare the partial pressure of masses 32 (O_2 + MeOH) and 31 (MeOH) in order to establish the gas phase composition during dosing. The images reported here are raw data, except for a simple global plane subtraction. They are not filtered or manipulated in any other way. Bias voltages quoted in the figure captions are sample biases relative to the tip.

STM and LEED have previously been employed to establish the adsorbed structures of oxygen, methoxy and formate on the Cu(110) surface [6, 15]. These may be considered as a library for the identification of adsorbates from reactions in phase separated systems. Oxygen preferentially forms a (2×1) added row reconstruction with alternating oxygen and copper atoms in the $\langle 001 \rangle$ direction [16, 17], although with very high exposures [18, 19] or with chemical compression [20] a distinctive higher coverage $c(6 \times 2)$ structure forms. Methoxy forms a single (5×2) structure also proposed to involve added copper atoms after reaction of methanol with a sub-saturation oxygen (2×1) surface [7, 14]. Formate adsorption is more complicated with the high-coverage $c(2 \times 2)$ structure forming with either
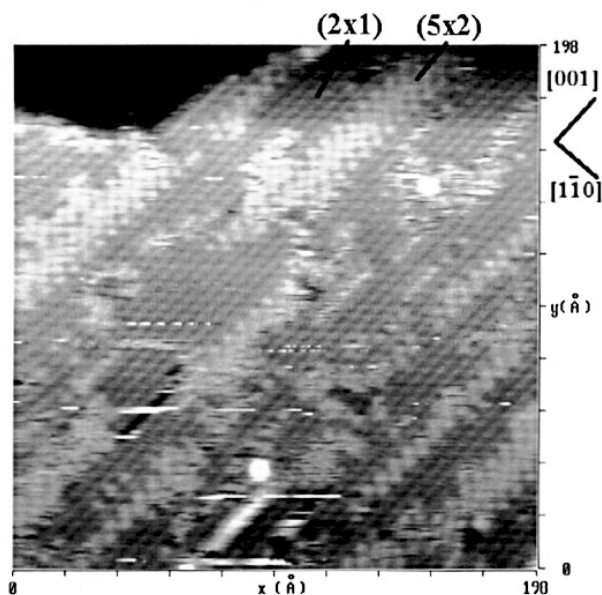
Figure 1. Competitive growth of methoxy (5×2) and oxygen (2×1) structures from an oxygen rich co-dosing (MeOH:O_2 of 1:1.4). Complete formation of the (5×2) island is restricted by the density of oxygen on the surface forcing methoxy to form zig-zag structures (imaged at 1 nA, -2 V, image size 198 Å square).

(3×1) at room temperature or (4×1) at elevated temperature (>330 K) after reaction of formic acid with the oxygen (2×1) reconstructed surface [15, 20]. The (3×1) and (4×1) structures are believed to incorporate added copper atoms released during reaction with the oxygen–copper rows. On clean Cu(110), formic acid adsorbs into a complex $(n \times 2)$ structure not observed in LEED due to poor long-range order.

The structure and therefore the chemical composition of the overlayer produced by co-adsorption of MeOH:O_2 mixtures on the clean Cu(110) surface changes substantially with the MeOH:O_2 gas phase ratio. For MeOH:$O_2 < 1$ i.e. oxygen in excess, there is an immediate and gradual increase in the coverage of the O (2×1) phase accompanied also by smaller areas of methoxy (5×2) which gradually diminish as O (2×1) increases with time (figure 1). As no methanol adsorption occurs at 300 K on the clean Cu(110) surface methoxy formation must result from methanol reaction with adsorbed oxygen ((1)–(3)) [21]. Sequential-dosing experiments have demonstrated that high O (2×1) coverages have very low activity for methoxy formation and so a rapid build up of large areas of O (2×1) can effectively lead to a poisoning of methoxy production [6]. There is therefore competition between build-up of the O (2×1) phase and reaction of the adsorbed oxygen to form methoxy. For MeOH:$O_2 < 1$ this competition favours build-up of O (2×1). For MeOH:$O_2 > 3$, i.e. methanol in excess, a crucial transition point is reached and there is no initial build-up of the O (2×1) phase. Instead a gradual build-up of the methoxy (5×2) is observed, forming increasingly large islands growing out from step edges until saturation of the surface. No O (2×1) is observed in STM as adsorbed oxygen atoms are consumed rapidly by methanol, preventing aggregation into (2×1) islands. Up to this point the reaction proceeds in essentially the same way as that produced by sequential-dosing experiments,
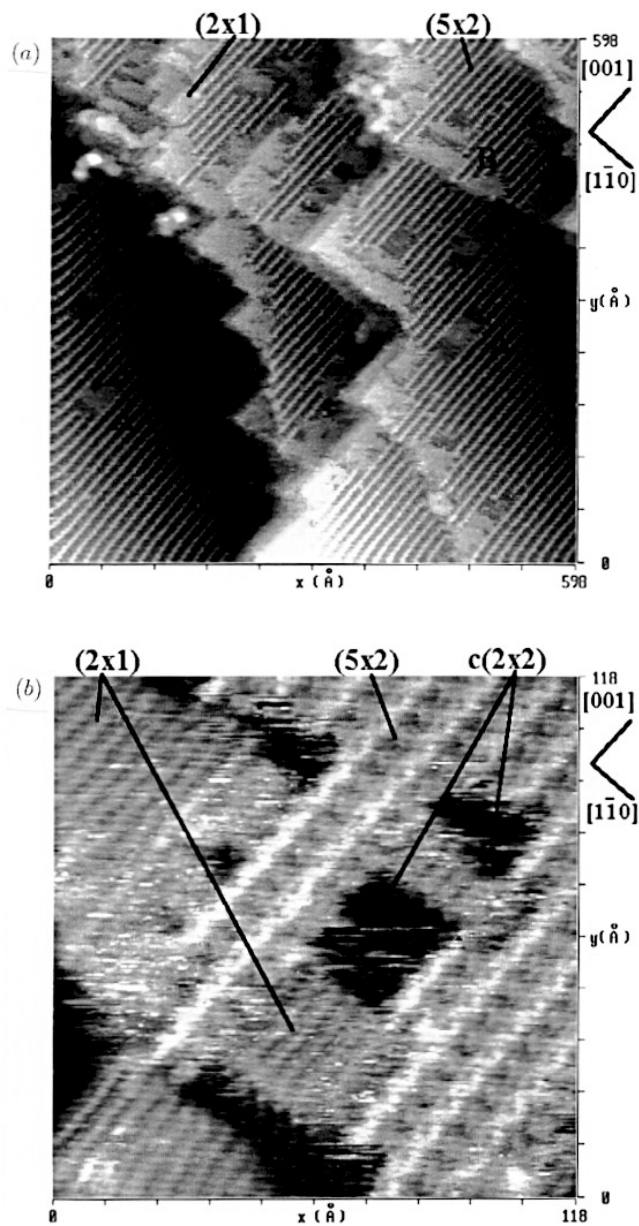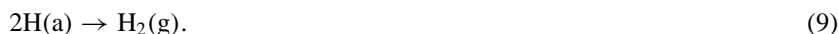
Figure 2. Island formation in the methoxy overlayer during co-dosing of an MeOH:O_2 mix of 3:1. (a) A large area (598 Å square) of the surface showing the growth of formate and oxygen (2 × 1) islands within the methoxy overlayer. The reactions are initiated both on terraces (A) and at step edges (B). Oxygen islands tend to predominate on the upper step edges. (1 nA, −500 mV.) (b) A close-up of a group of O (2 × 1) and formate c(2 × 2) islands showing the characteristic alternating growth pattern (1 nA, −500 mV, 118 Å square).

oxygen reacting with methanol to produce water and methoxy. However, after saturation of the surface with methoxy a new regime in the reaction and an alternative reaction pathway

is initiated. This new regime results in the formation of islands of c(2 × 2) structure within the methoxy overlayer which originally covered the whole surface (figure 2(a)). We assign these c(2 × 2) regions to adsorbed formate, this structure previously having been observed for the formate overlayer produced by formic acid adsorption on $O_{0.25\,ML}$/Cu(110) [15]. These formate areas are accompanied by the simultaneous build-up of adjacent O (2 × 1) areas (figure 2(b)). With increasing exposure the coverage of both the formate c(2 × 2) and O (2 × 1) increase though in our experiments the methoxy (5 × 2) is never completely replaced. The production of formate in this co-dosing experiment is confirmed by TPD which reveals a CO_2 desorption peak at 480 K, consistent with formate decomposition as reported by others [15, 22, 23]. Furthermore, as mentioned below, a (3 × 1) structure can also be obtained during co-dosing of methanol and oxygen. This structure is again observed for formic acid adsorption on oxygen precovered Cu(110) and has been identified with the formate component of the overlayer [15].

We propose that the crucial requirement for formate generation is the creation of isolated adsorbed oxygen atoms within the methoxy overlayer. These react either directly with methoxy groups, or more probably, with formaldehyde which is generated by the decomposition of methoxy ((4)–(9)). Even at 300 K methoxy decomposition to formaldehyde is known to occur at a significant rate on the time scale of this experiment (up to 1 h) [24] and additional oxygen induced decomposition may occur to generate formaldehyde at a high enough rate to account for the formate production observed. The reaction between formaldehyde and oxygen to produce formate on Cu(110) occurs readily and has previously been reported [23].

$$CH_3O(a) \rightarrow H_2CO(a) + H(a) \tag{4}$$

$$H_2CO(a) \rightarrow H_2CO(g) \tag{5}$$

$$H_2CO(a) + O(a) \rightarrow H_2COO(a) \tag{6}$$

$$H_2COO(a) \rightarrow HCOO(a) + H(a) \tag{7}$$

$$2H(a) + O(a) \rightarrow H_2O(g) \tag{8}$$

$$2H(a) \rightarrow H_2(g). \tag{9}$$

It is interesting to note that islands of formate and oxygen grow alongside each other and so a proposed mechanism must account for this. A likely explanation rests in the different adatom densities of the phases produced. The methoxy phase has a local density of 0.4 ML and both oxygen and formate c(2 × 2) have a density of 0.5 ML. Thus consumption of methoxy and replacement with oxygen or formate leads to the creation of clean surface at which both oxygen adsorption and methoxy decomposition are accelerated. Though some of this oxygen will react to produce formate some of the adsorbed oxygen in this region also aggregates into the (2 × 1) phase which acts as a nucleus for oxygen island growth. At this temperature the (2 × 1) island acts as a sink for the reactive oxygen adatom species which subsequently quenches the rate of formate production. Methanol attack at the ends of the (2 × 1) island rows is inhibited by the lack of clean surface for adsorption. This slow trimming of the ends of the rows forces a change in the aspect ratio of the oxygen islands in comparison to those on the clean surface, i.e. from long narrow chains to short wide segments.

For an MeOH:O_2 ratio of ∼5:1 [25] areas of c(2 × 2) formate larger than those shown in figure 2 are observed with little O (2 × 1) growth (figure 3(a)) and with continued dosing (∼ 1 × 10³ L) a formate (3 × 1) phase is produced (figure 3(b)). The activity of the oxygen in this case is higher because of its lower concentration on the surface, prohibiting formation of (2 × 1) islands which capture oxygen adatoms and consequently poison the
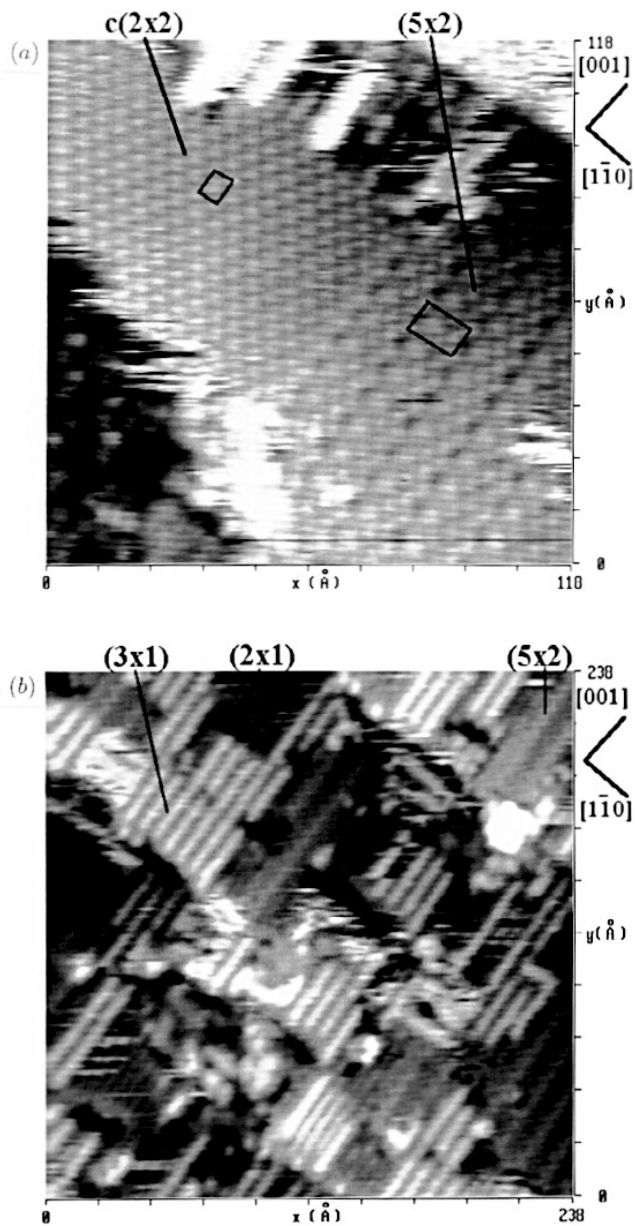
Figure 3. (a) Formate c(2 × 2) grown alongside a methoxy (5 × 2) area as a result of co-dosing a methanol rich mixture (MeOH:O$_2$ of greater than 5:1 [25]) to the surface (1 nA, −2 V, 118 Å square). Unit cells of c(2 × 2) and (5 × 2) are marked. (b) Continued dosing leads to formate (3 × 1) islands gradually replacing the c(2 × 2) and oxygen (2 × 1) structures (1 nA, −500 mV, 238 Å square).

formate production.

In summary we have shown that the co-dosing of methanol and oxygen onto Cu(110) at 300 K generates an alternative reaction mechanism to that which dominates during

sequential dosing, namely formate production. This alternative reaction mechanism is proposed to arise from the reaction of isolated oxygen adatoms in a methoxy overlayer. We have demonstrated the utility of STM in identifying both temporal and spatial aspects of a catalytic reaction. These results illustrate the molecular level complexity that arises in notionally simple macroscopic reactions.

References

[1] Wachs I and Madix R J 1978 *J. Catal.* **53** 208
[2] Bowker M and Madix R J 1980 *Surf. Sci.* **95** 190
[3] Wachs I and Madix R J 1978 *Surf. Sci.* **76** 531
[4] Madix R J and Telford S G 1995 *Surf. Sci.* **328** L576
[5] Bowker M 1994 *Surf. Rev. Lett.* **1** 549
[6] Francis S M, Leibsle F M, Haq S, Xiang N and Bowker M 1994 *Surf. Sci.* **315** 284
[7] Leibsle F M, Francis S M, Haq S and Bowker M 1994 *Surf. Sci.* **318** 46
[8] Carley A F, Owens A W, Rajumon M K, Roberts M W and Jackson S D 1996 *Catal. Lett.* **37** 79
[9] Carley A F, Davies P R, Mariotti G G and Read S 1996 *Surf. Sci.* **364** L525
[10] Crew W W and Madix R J 1996 *Surf. Sci.* **349** 275
[11] Sueyoshi T, Sasaki T and Iwasawa Y 1996 *Surf. Sci.* **357/358** 764
[12] Sueyoshi T, Sasaki T and Iwasawa Y 1995 *Chem. Phys. Lett.* **241** 189
[13] Afsin B, Davies P R, Pashusky A, Roberts M W and Vincent D 1993 *Surf. Sci.* **284** 109
[14] Jones A H, Poulston S, Bennett R A and Bowker M *Surf. Sci.* submitted
[15] Bowker M, Rowbotham E, Leibsle F M and Haq S 1996 *Surf. Sci.* **349** 97
[16] Wintterlin J, Schuster R, Coulman D J, Ertl G and Behm R J 1991 *J. Vac. Sci. Technol.* B **9** 902
[17] Kern K, Niehus H, Schatz A, Zeppenfeld P, George J and Comsa G 1991 *Phys. Rev. Lett.* **67** 855
[18] Feidenhans'l R, Grey F, Nielsen M, Besenbacher F, Jensen F, Laegsgaard E, Stensgaard I, Jacobsen K W, Nørskov J K and Johnson R L 1990 *Phys. Rev. Lett.* **65** 2027
[19] Coulman D J, Wintterlin J, Barth J V, Ertl G and Behm R J 1990 *Surf. Sci.* **240** 151
[20] Poulston S, Jones A, Bennett R A and Bowker M *Surf. Sci.* submitted
[21] Barnes C, Pudney P, Guo Q and Bowker M 1990 *J. Chem. Soc. Faraday Trans.* **86** 2693
[22] Ying D and Madix R J 1980 *J. Catal.* **61** 48
[23] Bowker M and Madix R J 1981 *Surf. Sci.* **102** 542
[24] Bowker M and Leibsle F M 1996 *Catal. Lett.* **38** 123
[25] Accurate measurement of the mixture composition is hampered by the cracking pattern of the methanol to mass 32 amu. The quoted figure represents the estimated upper limit of the methanol to oxygen ratio.