The two states of methoxy at Cu(110) surfaces identified

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The coadsorption of methanol rich, dioxygen–methanol mixtures at Cu(110) surfaces is shown to result in an adlayer consisting entirely of a single state of chemisorbed methoxy species; this confirms that a second more strongly adsorbed state of methoxy, observed in the presence of preadsorbed oxygen, is stabilised by the chemisorbed oxygen.

Methanol oxidation at copper surfaces is a model reaction which has considerable relevance to the industrial synthesis of methanol and formaldehyde. It has therefore been studied in great detail by many researchers.[1–6] However it remains a subject of some controversy and two recent developments have stimulated more discussion in this area. First, XPS[7] and TPD[8,9] studies have shown that in addition to the conventionally accepted pathway to formaldehyde desorption [steps (1)–(4)], methanol may also be oxidised further on copper surfaces to yield formate [step (5)]. Secondly, STM has shown that there is extensive islanding of both the chemisorbed oxygen and the methoxy species at Cu(110) surfaces at room temperature.[10,11]

$$2\text{MeOH(g)} + \text{O}^{\delta-}\text{(a)} \rightarrow 2\text{MeO(a)} + \text{H}_2\text{O(g)} \quad (1)$$

$$\text{MeO(a)} \rightarrow \text{H}_2\text{CO(a)} + \text{H(a)} \quad (2)$$

$$\text{H}_2\text{CO(a)} \rightarrow \text{H}_2\text{CO(g)} \quad (3)$$

$$2\text{H(a)} \rightarrow \text{H}_2\text{(g)} \quad (4)$$

$$\text{H}_2\text{CO(a)} + \text{O}^{\delta-}\text{(a)} \rightarrow \text{HCO}_2\text{(a)} + \text{H(a)} \quad (5)$$

We discuss elsewhere[12] the role of the oxygen and methoxy islands in determining the reaction pathway of methanol oxidation on copper and the specific conditions under which *either* formate *or* formaldehyde can be the major products of the reaction. In the present paper we address the unresolved question of the identities of the two states of methoxy produced from the adsorption of methanol at a preoxidised Cu(110) surface at 180 K and reported by Wachs and Madix in 1978.[1] The two states are evident from TPD results which show the desorption of formaldehyde [*via* step (2)] at two distinct temperatures (*ca.* 350 and 375 K) depending upon the methanol exposure—high exposures favouring the least stable methoxy state.

In Fig. 1 we show that two states of methoxy can also be formed at room temperature. We find that low initial oxygen coverages favour the least stable methoxy state [Fig. 1(*a*)], whereas high initial oxygen coverages favour the more stable state [Fig. (1*c*)]. For intermediate coverages of oxygen the two methoxy states coexist [Fig. 1(*b*)]. This strongly suggests that the stability of the second methoxy state is due to the presence of chemisorbed oxygen. This would be consistent with Wachs and Madix's observations since high exposures of methanol would reduce the surface concentration of chemisorbed oxygen *via* step (1).

To investigate the effect of chemisorbed oxygen further we need to generate a high coverage of methoxy under conditions where the chemisorbed oxygen concentration is negligible. To achieve this we have coadsorbed methanol and dioxygen mixtures. The coadsorption approach has been shown in the analogous NH_3–O_2[13,14] and H_2O–O_2[15] systems to result in highly specific product formation, virtually complete monolayers of NH(a) and OH(a) being obtained in the two systems with no evidence for chemisorbed oxygen. We have suggested[14] that this specificity is due to the inhibition of oxygen island growth during coadsorption and the unusually high reactivity of the resulting 'isolated' oxygen adatoms. Fig. 2(*b*) shows that a similar specificity can be obtained in the CD_3OH–O_2 system using methanol rich mixtures. A clean Cu(110) surface was exposed to a 20 : 1 methanol–dioxygen mixture for 30 min. In the resulting TPD spectrum formaldehyde is the major product and gives an unusually sharp desorption peak at *ca.* 345 K. The contrast between this spectrum and that recorded following exposure of a preoxidised surface ($\theta_O \approx 0.25$) to methanol, Fig. 2(*a*), is striking. It is immediately clear that only a single methoxy state can be present after coadsorption at the clean surface.

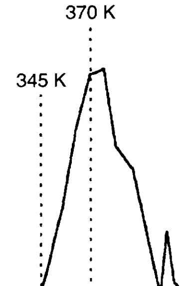

Fig. 1 The effect of oxygen coverage on the stability of methoxy species at Cu(110) surfaces. The spectra show the temperature programmed desorption of deuteriated formaldehyde (D_2CO, *m/z* 30) from the surface after different initial coverages of oxygen were exposed to deuteriated methanol (CD_3OH) at 290 K for 5 min at *ca.* 10^{-8} mbar. Oxygen coverages are estimated to be (*a*) 0.1, (*b*) 0.25, (*c*) 0.5 monolayers. See ref. 9 for further experimental details.

To explore the role of chemisorbed oxygen further we have investigated the effect of preadsorbed oxygen on the coadsorption experiment. A preoxidised Cu(110) surface ($\theta_O \approx 0.2$) was exposed to the 20:1 methanol–dioxygen mixture. The resulting TPD spectrum, Fig. 2(*c*), shows very clearly the development of the second methoxy state establishing unequivocally the role of chemisorbed oxygen in stabilising methoxy species at the surface.

STM images in the literature[10,11,16] provide evidence for at least two states of methoxy at preoxidised copper surfaces at room temperature, an islanded phase and a mobile phase, the presence of the latter being deduced from the transport of methoxy species across the surface rather than by direct imaging. It has been suggested[17] that these two methoxy states correspond to the two states evident in the TPD spectra. The present results are not consistent with this interpretation however, rather they indicate that the more stable state is due to methoxy species stabilised by interaction with chemisorbed oxygen. In fact the STM images do indicate an overall diffusion of species from the methoxy islands to the edges of the (2 × 1) O(a) islands, we can interpret this as an equilibration process in which the methoxy species move towards a more stable state, thus supporting our hypothesis.

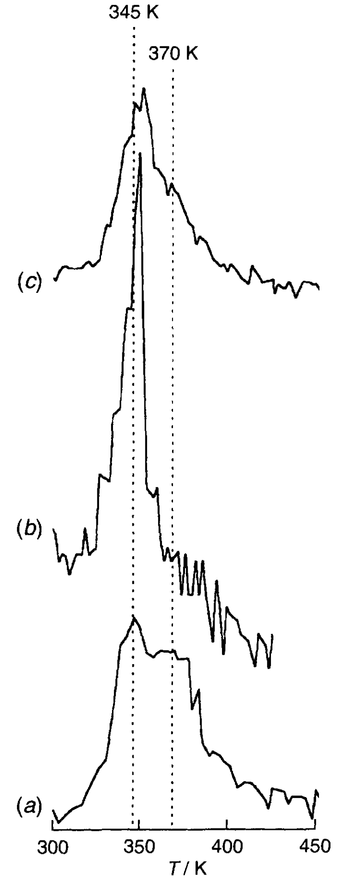

Fig. 2 The coadsorption of deuteriated methanol and dioxygen at Cu(110) surfaces. TPD spectra for *m*/*z* 32 (D_2CO) are shown for (*a*) preoxidised Cu(110) ($\theta_O \approx 0.25$) exposed to deuteriated methanol for 5 min [as (*b*) in Fig. 1]; (*b*) clean Cu(110) exposed to a 20:1 methanol–dioxygen mixture for 30 min, (*c*) preoxidised Cu(110) ($\theta_O \approx 0.2$) exposed to a 20:1 methanol–dioxygen mixture for 6 min.

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Footnote

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