Controlling reaction selectivity in the oxidation of methanol at Cu(110) surfaces

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When deuterated methanol (CD_3OH) and dioxygen mixtures are coadsorbed at Cu(110) surfaces at room temperature and above, the main reaction product can be switched between formaldehyde and formate by changing the mixture composition. For oxygen-rich mixtures formaldehyde is the major product but when methanol is in 5 : 1 excess only formate is produced. It is proposed that the reaction mechanism is controlled by the microscopic structure of the surface: when the reactants are adsorbed sequentially, separate islands of oxygen and methoxy develop which inhibit further oxidation but when reactants are coadsorbed a homogeneous mixture of adsorbates is produced creating a facile pathway to formate.

Keywords: methanol, oxidation, copper, desorption

1. Introduction

Surface science has had an enormous impact on our understanding of the fundamental processes underlying many catalytic reactions. However, detailed mechanisms have often been proposed on the basis of surface science experiments performed under a very narrow range of conditions. The oxidation of methanol at copper surfaces, an important model system with considerable technological relevance, illustrates the dangers inherent in this approach. We show here that the pathway taken by the methanol oxidation reaction at copper surfaces is very sensitive to the experimental conditions. In particular, we establish that formate, which for many years was believed not to be produced from this reaction, is the only product under some conditions.

$$2CH_3OH(g) + O^{\delta-}(a) \rightarrow 2CH_3O(a) + H_2O(g) \quad (1)$$

$$CH_3O(a) \rightarrow H_2CO(a) + H(a) \quad (2)$$

$$H_2CO(a) \rightarrow H_2CO(g) \quad (3)$$

$$2H(a) \rightarrow H_2(g) \quad (4)$$

$$H_2CO(a) + O^{\delta-}(a) \rightarrow HCO_2(a) + H(a) \quad (5)$$

$$HCO_2(a) \rightarrow CO_2(g) + H(a) \quad (6)$$

The accepted mechanism for methanol oxidation at copper surfaces, the main points of which are summarised in steps (1)–(6), has only recently been updated to include oxidation to formate (steps (5) and (6)). These steps were added after XPS [1] and TPD [2–4] results showed that formate is produced at Cu(110) surfaces from a mixed methoxy and chemisorbed oxygen adlayer over a period of an hour or more; the slow rate of reaction having prevented the observation of formate in previous studies [5,6].

We have suggested [3] that the oxidation of methoxy species to formate is inhibited on Cu(110) by the formation of methoxy islands. Such adsorbate island growth can be prevented by dosing reactants to the surface simultaneously instead of sequentially, the reactive "isolated" chemisorbed species being removed before they become incorporated into unreactive islands. This approach can lead to unusually selective and efficient reaction pathways; for example, OH(a) and NH(a) can be formed exclusively and in near-monolayer concentrations from H_2O/O_2 and NH_3/O_2 mixtures at Cu(111) [7] and Cu(110) [8] surfaces respectively.

In the present paper we use the coadsorption strategy to explore in more detail the role of methoxy and oxygen islands in methanol oxidation at copper surfaces. The results show that catalytic selectivity can be controlled by changing the ratio of reactants in the gas mixture.

2. Experimental

The experiments were carried out in a system equipped with a Ledamass multiquad spectrometer which enables up to seven masses to be recorded simultaneously. Data was acquired by software written in house. The dimensions of the sample were approximately 10 mm by 7 mm with a thickness of approximately 1/2 mm, it was cut to within 0.5° of the (110) plane and polished mechanically down to 0.25 μm. Four holes approximately 0.5 mm in

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diameter were spark-eroded in the corners and the sample suspended by two tungsten wires threaded through the holes. The temperature of the sample was measured with a chromel–alumel thermocouple secured by silver epoxy resin in a notch cut into the back of the sample. Cleaning involved cycles of Ar^+ sputtering (5 keV, 10 $\mu A/cm^2$ for 10 min) and annealing 10–20 min 1000 K, conditions that give consistently good results in other spectrometers within our group. The sample cleanliness was confirmed by TPD spectra which reproduced previous results. The sample was warmed by resistive heating of the tungsten support wires. A heating rate of 4 K/s was used in all the experiments in this study.

Gases were introduced to the sample via a glass capillary that could be placed directly in front of the sample face. During dosing the system pressure did not increase above 10^{-8} Torr. This method of gas dosing gave very reproducible results although exact exposures cannot be calculated precisely. Gases could also be introduced to the chamber by backfilling via a variable leak valve. In the coadsorption experiments methanol vapour and dioxygen gas were allowed to mix in a separate volume for at least an hour before dosing and the mixture ratio tested by mass spectrometer before and after each dose.

The deuterated methanol (CD_3OH, Aldrich 99%) was placed in a sample tube attached to the spectrometer, dissolved gases were removed with several freeze–pump–thaw cycles and the purity checked by mass spectrometry. As a further check the methanol was physisorbed at the clean Cu(110) surface at 100 K and desorbed in a TPD experiment. Only methanol was observed desorbing from the sample during this experiment, there was no evidence for contamination due to formaldehyde (desorption temperature ~ 220 K), water (desorption temperature ~160 K) or dioxygen.

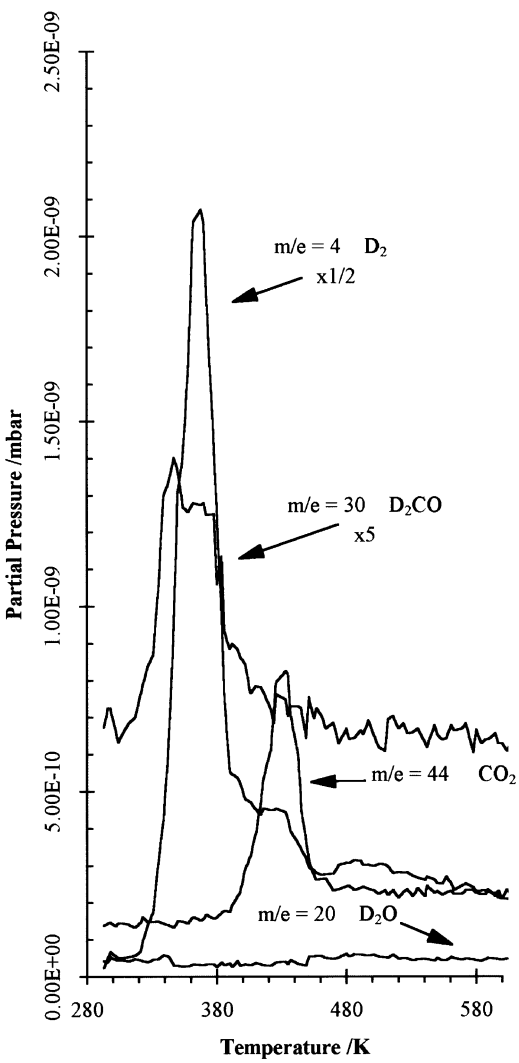

Fig. 1. Temperature-programmed desorption spectra recorded simultaneously from a partially oxidised Cu(110) surface (240 s $O_2(g)$ at 290 K) immediately after exposure (300 s) to deuterated methanol (CD_3OH) at 290 K. We estimate [3] the oxygen precoverage to be close to 0.25 monolayers.

3. Results

3.1. The reaction of methanol with preadsorbed oxygen

Fig. 1 shows a typical set of TPD spectra recorded from a preoxidised Cu(110) sample ($\theta_O \approx 0.25$) after deuterated methanol adsorption at 290 K. The strongest desorption signals observed are at $m/e = 4$, 30 and 44 and are due to the principal fragments of D_2, D_2CO and CO_2 respectively. These desorbing species arise from the decomposition of chemisorbed methoxy ($CD_3O(a)$) and of formate ($DCO_2(a)$), the latter being observed in significant quantities only when methanol is adsorbed at room temperature or above. A much weaker signal is also observed (between 340 and 375 K) at $m/e = 36$ due to recombination and desorption of deuterated methanol (CD_3OD) but there is no desorption of deuterated water ($m/e = 20$). Formaldehyde desorption occurs at two temperatures, ~ 345 K and 370 K, indicating the presence of at least two states of chemisorbed methoxy. The more strongly chemisorbed state has been shown [4] to be due to methoxy species stabilised by interactions with chemisorbed oxygen. The principal peak in the D_2 desorption spectrum is at ~ 375 K but there is also a small shoulder at 430 K coincident with the CO_2 desorption peak. Coincident D_2 and CO_2 desorption peaks are a characteristic of adsorbed formate. The ratio of the two D_2 desorption peaks gives an idea of the relative importance of the formaldehyde and formate pathways in methoxy decomposition. We estimate in the present case that about 20% of the total methoxy is oxidised to formate.

3.2. The reaction of methanol with coadsorbed oxygen and the influence of the mixture ratio

The TPD spectra in fig. 2 were recorded after a

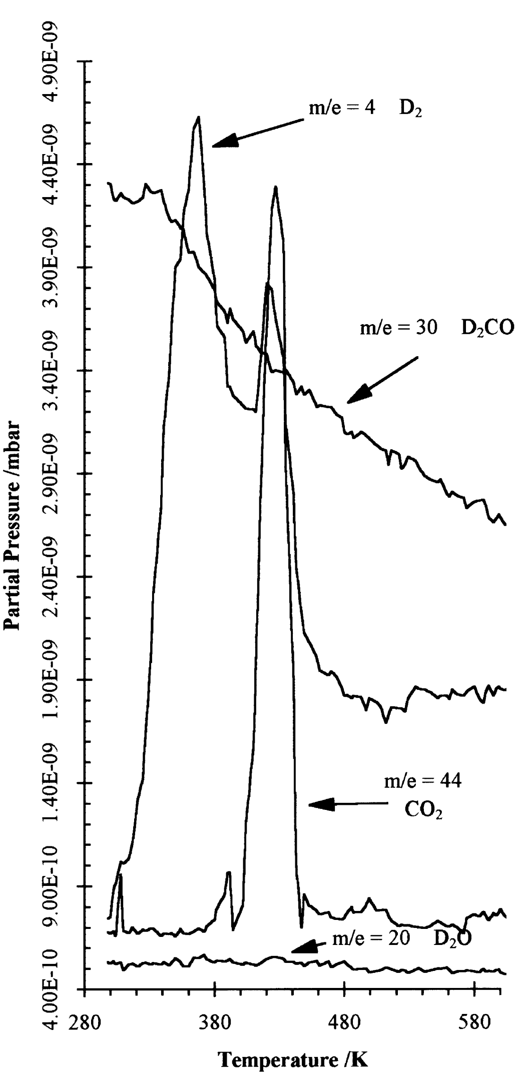

Fig. 2. Temperature-programmed desorption spectra recorded simultaneously from a clean Cu(110) surface immediately after exposure (300 s) to a 5 : 1 deuterated methanol (CD_3OH)/dioxygen mixture at $\sim 10^{-8}$ mbar and 300 K.

Cu(110) surface was exposed to a 5 : 1 methanol/dioxygen mixture at 300 K and show a number of notable changes from the spectra in fig. 1. The formaldehyde peak is only just apparent above the background whereas the CO_2 signal, due to formate decomposition, is at least five times stronger than the maximum CO_2 signal observed when oxygen is preadsorbed. The D_2 desorption spectrum also reflects a very high surface concentration of formate with the desorption peak at 430 K having almost half the intensity of the 375 K peak. Since the formation of formate (between 300 and 370 K) produces two atoms of deuterium whereas the decomposition of formate at 430 K releases only one,

$$CD_3O(a) + O^{\delta-}(a) \xrightarrow{330-370\,K} DCO_2(a) + D_2(g) \qquad (7)$$

$$DCO_2(a) \xrightarrow{430\,K} CO_2(g) + \tfrac{1}{2}D_2(g) \qquad (8)$$

this confirms that formate is the only significant product of methanol oxidation under coadsorption conditions.

It is important to recall at this point that TPD cannot distinguish easily between a pure formate adlayer and a mixed chemisorbed oxygen and methoxy adlayer that converts to formate during the TPD heating ramp. It is unlikely, however, that in the latter case a complete conversion to formate could be achieved below 330–370 K (the decomposition temperature of surface methoxy) without considerable reaction occurring at 300 K. Whether this is the case or not, it is abundantly clear that when methanol and dioxygen are coadsorbed, a very facile pathway to formate exists, one that is not available when dioxygen is preadsorbed.

Fig. 3 shows $m/e = 30$, 44 and 4 desorption signals for a selection of experiments which explore the influence of the methanol/dioxygen mixture ratio on the products of the coadsorption reaction. For comparison the TPD spectra of fig. 1 (oxygen preadsorption) are also included in the diagram. For a 2 : 1 mixture the spectra resemble those observed from the preoxidised surface reasonably closely, the main difference being the unusually sharp formaldehyde desorption peak at 345 K. The latter suggests that there is little chemisorbed oxygen remaining at the surface since the presence of chemisorbed oxygen leads to a more strongly chemisorbed methoxy species which desorbs at $\sim$ 370 K [4]. As the mixture is made richer in methanol there is a rapid decrease in the area of the formaldehyde desorption peak and a corresponding increase in that of the carbon dioxide peak. For methanol/dioxygen mixture ratios of about 5 to 1 very little formaldehyde desorbs from the surface and, as noted above, formate is clearly the dominant surface species. As the methanol component of the mixture is increased further however, the surface concentration of formate is reduced and the area of the formaldehyde desorption peak increases indicating higher surface concentrations of methoxy. For a 20 : 1 mixture the formaldehyde desorption peak is again strong despite the relatively low total exposure to oxygen. Formate on the other hand is present only at a low concentration. A more quantitative assessment of the changes in the reaction products is presented in fig. 4, which plots the ratio of the $m/e = 30$ and $m/e = 44$ peak areas against mixture composition. The chart confirms the qualitative discussion above, showing a dramatic change in the reaction pathway with mixture composition.

An interesting observation from these experiments is that as the methanol/dioxygen mixture ratio is increased the principal deuterium desorption peak shifts from $\sim$ 370 to $\sim$ 330 K. Hydrogen is known [9] to desorb from clean copper surfaces at $\sim$ 330 K but in the presence of a mixed dioxygen/methoxy adlayer remains at the surface until $\sim$ 370 K [3,10]. The reason for this is not known but has been suggested [11] to be associated with the oxygen induced reconstruction of the surface. The present

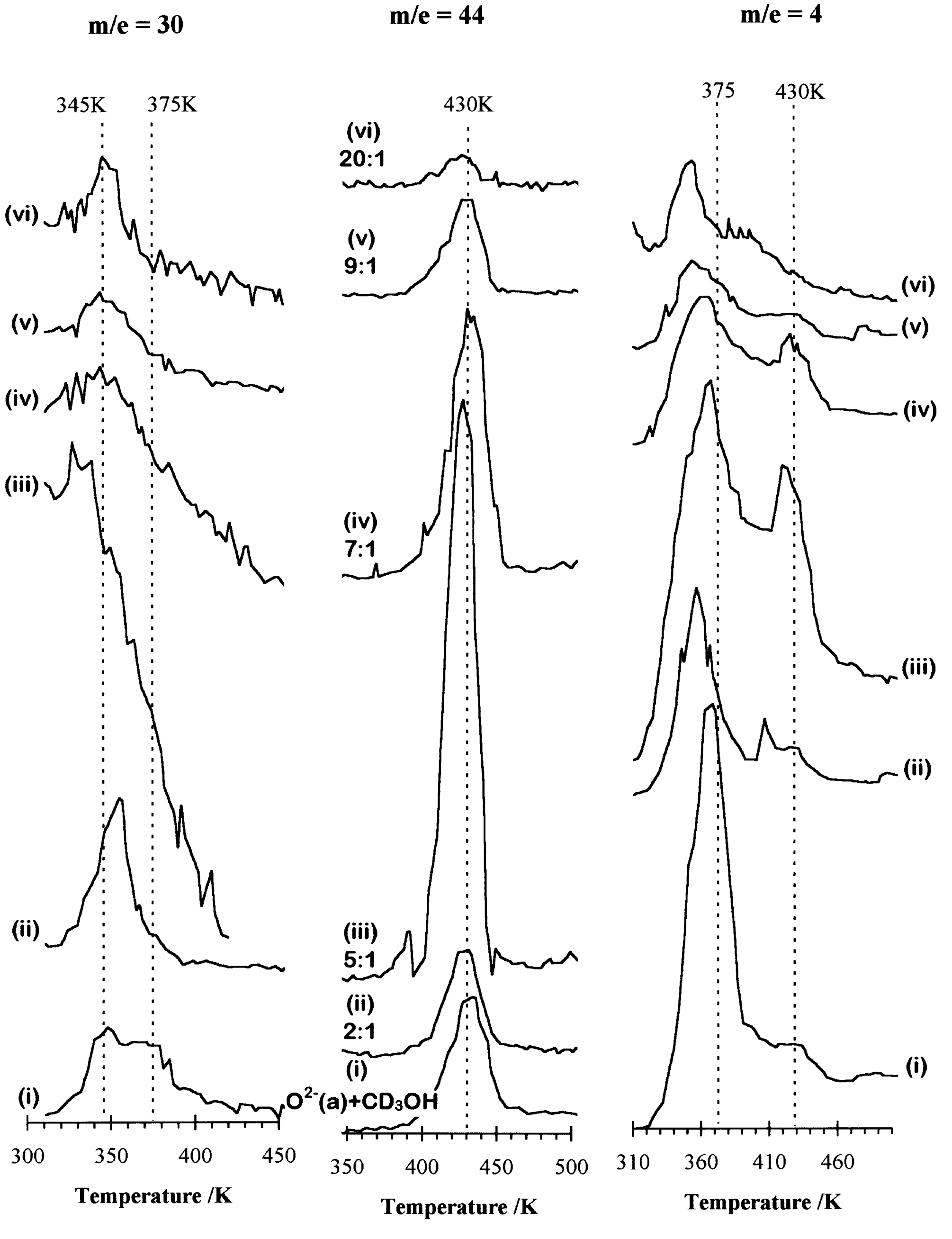

Fig. 3. The effect of mixture composition on the reaction of deuterated methanol (CD_3OH)/dioxygen mixtures at a Cu(110) surface at 300 K. Formaldehyde, carbon dioxide and deuterium desorption spectra were recorded simultaneously from a clean Cu(110) surface immediately after a 300 s exposure at a total pressure of ca. 10^{-8} mbar to mixtures with CD_3OH/O_2 ratios of (ii) 2 : 1; (iii) 5 : 1; (iv) 7 : 1; (v) 9 : 1 and (vi) 20 : 1. For comparison the spectra from fig. 1 are also included in the figure and labelled spectrum (i).

results would be consistent with that theory since the rapid rate of oxygen removal at high methanol mixture ratios would prevent reconstruction.

3.3. The effect of temperature

Fig. 5A shows the $m/e = 44$ desorption spectra recorded after a *preoxidised* copper surface was exposed to a fixed dose of methanol at three different temperatures. There is a large increase in the concentration of formate at higher temperatures. This increase can be ascribed chiefly to an increase in the rate constant for the reaction since the (2 × 1) oxygen islands are relatively stable at 400 K [12] and hence the concentration of active sites will not be changed significantly at the higher temperatures. The activation energy calculated from an Arrhenius plot of this data is 20 kJ/mol. In contrast when methanol and dioxygen are coadsorbed, fig. 5B, the quantity of formate produced is unaffected by the temperature of the sample. This indicates that the oxidation of methoxy to formate under these conditions is much more facile and

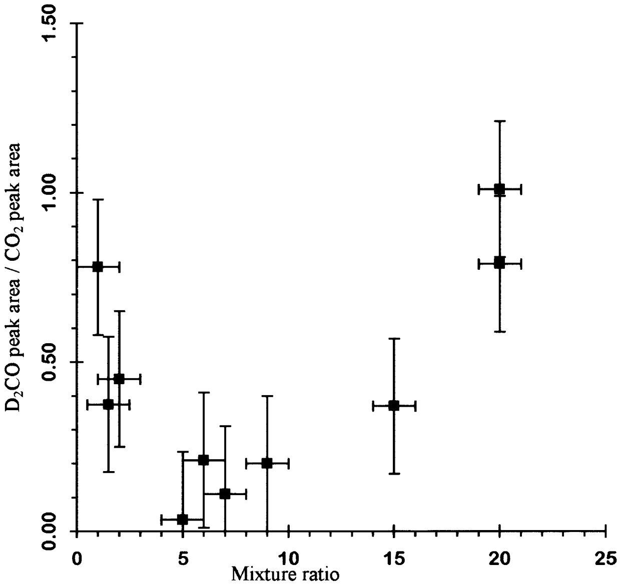

Fig. 4. The effect of mixture composition on the products of methanol oxidation from coadsorbed deuterated methanol/dioxygen mixtures. The ratio of formaldehyde peak area/carbon dioxide peak area is plotted as a function of mixture ratio. Error bars are estimated from the reproducibility of experimental measurements.

provides an insight into the nature of the oxygen species in the two experiments.

4. Discussion

The rate of formate formation from the reaction of methanol with preadsorbed oxygen is slow at room temperature. On the basis of TPD experiments at different temperatures and a comparison between TPD and XPS results we have argued [3,4] that the products observed by TPD for this system are controlled principally by the formation of islands of methoxy molecules and the rate of transport of methoxy from the islands to the active oxidation sites. Below room temperature extensive methoxy island formation restricts access to the active oxidation sites hence formate is not observed in TPD experiments. At room temperature and above, a mobile methoxy phase provides access to the active sites and oxidation to formate becomes a significant pathway.

The principal observation from the present results is that the coadsorption of mixtures of methanol and dioxygen at a Cu(110) surface opens up a much more facile pathway to formate than is available when oxygen is preadsorbed. Furthermore different selectivities to either formaldehyde or formate can be obtained by changing the composition of the reaction mixture. For dioxygen-rich mixtures, formaldehyde desorption dominates but as the dioxygen component of the mixture is decreased there is an increase in the extent of oxidation until, for methanol/oxygen mixture ratios of around 5 to 1, formate is virtually the only surface species produced by the reaction. Decreasing the partial pressure of the dioxygen component further, however, leads to a decrease in the proportion of formate formed.

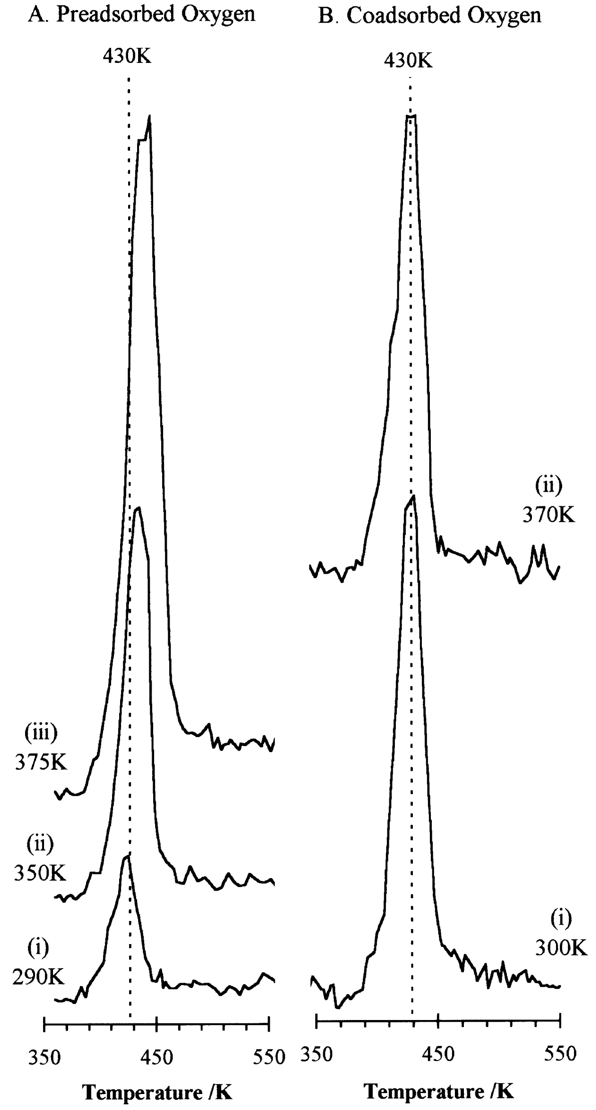

Fig. 5. The effect of temperature on the surface concentration of formate produced from the oxidation of methanol on Cu(110). (A) Preoxidised Cu(110) ($\theta_O \approx 0.05$) exposed to 300 s deuterated methanol; (i) 290 K; (ii) 350 K; (iii) 370 K; (B) a 2 : 1 methanol/dioxygen mixture coadsorbed (300 s) at (i) 300 K; (ii) 370 K.

These results are consistent with the formation of formate being controlled principally by the presence of chemisorbed *oxygen* islands. In an oxygen-rich mixture, chemisorbed oxygen island growth is favoured and formate formation inhibited by the lack of reactive sites, the majority of oxygen adatoms within the islands being unreactive. As the dioxygen concentration in the mixture is decreased the average size of oxygen islands also decreases, resulting in an increase in the availability of sites for methanol and methoxy oxidation. For mixtures with ratios of about 5 : 1, the number of sites is sufficiently large that all of the methoxy species can be converted to formate. Under these conditions the reaction effectively creates its own reactive sites by maintaining the oxygen concentration close to zero. If the mixtures are made even richer in methanol however, the formation of formate is hindered by the low surface concentration of oxygen. In this case oxygen adatoms created at the surface are more likely to encounter adsorbed methanol molecules than methoxy species and hence methoxy is (initially) the major product.

In addition to controlling the availability of reaction sites however, the coadsorption of methanol and dioxygen also allows the participation of short-lived transients such as molecular oxygen and the so-called "hot" oxygen atoms [13]. Such species have been shown to play key roles in reactions at magnesium [14], aluminium [15] and zinc [16] surfaces and have been linked with highly efficient processes on copper [7,8] and nickel [17]. There is also evidence [18–21] that oxygen adatoms on an unreconstructed surface are more reactive than their reconstructed counterparts. The oxygen species involved in methanol oxidation will depend upon the precise reaction conditions. Therefore the effect of changing the mixture ratio may be to select for different oxygen states.

5. Conclusions

The selectivity of methanol oxidation at Cu(110) surfaces can be controlled and the main reaction product switched from formaldehyde to formate. Methanol and dioxygen mixtures with ratios of about 5 : 1 (methanol/dioxygen) produce only formate whereas preadsorbed oxygen, dioxygen-rich mixtures (1 : 1) and methanol-rich mixtures (20 : 1) give formaldehyde as the major product.

The change in reaction product with experimental conditions can be attributed to the sensitivity of the mechanism to the local atomic structure which is itself controlled by the oxidation reaction. When oxygen is preadsorbed or when it is the major component of a mixture, separate islands of methoxy and chemisorbed oxygen develop. These unreactive islands limit interaction between the adsorbed species and hence favour the formation of formaldehyde. If methanol is present in high enough concentrations however, the rapid removal of chemisorbed oxygen prevents the formation of unreactive islands. This creates an intimate mixture of methoxy and chemisorbed oxygen favouring the formation of formate.

The present results not only provide a new insight into the mechanism of the oxidation of methanol at copper surfaces, they may also have a more general significance for our understanding of selectivity in heterogeneous catalysis.

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