Temperature-programmed desorption studies of methanol and formic acid decomposition on copper oxide surfaces

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We have obtained temperature-programmed desorption data for methanol and formic acid adsorption on bulk powders of CuO and Cu_2O. Methanol adsorption on CuO at 300 K results in CO_2, H_2 and H_2O desorption at 550 K indicating formate decomposition; this decomposition temperature is very close to that obtained from the decomposition of formate produced by formic acid adsorption. No significant desorption was observed from vacuum-annealed Cu_2O following exposure to methanol due to the formation of a copper metal film at the surface. However, formic acid was adsorbed on this surface decomposing at significantly lower temperature, 485 K, than on CuO.

Keywords: copper, copper oxide, methanol, formic acid

1. Introduction

The adsorption and decomposition of formic acid and methanol on copper surfaces has been the subject of a considerable amount of research with a range of substrates including copper single crystals [1–19], supported Cu catalysts [20–27] and bulk copper oxides [28]. The work is motivated, in part, by the use of copper-based catalysts in methanol synthesis. Formate has been implicated as a key intermediate in this reaction [29], and so some work has focused on formic acid adsorption which produces formate species. Other work has been concerned with the interaction of methanol, CO_2 and H_2 with copper surfaces. Methanol adsorption on Cu(110) single-crystal surfaces precovered with chemisorbed oxygen produces methoxy species which decompose mainly to formaldehyde on heating to 360 K [16,30]. Small amounts of formate can also be produced, the exact amount depending on the details of the adsorption/desorption procedure [30–40]. In particular, if Cu(110) is simultaneously exposed to methanol and oxygen at 300 K, substantial amounts of formate can be produced compared with the sequential dosing of oxygen then methanol [35–37]. A recent study by Harikumar and Rao [41] examined the adsorption of methanol on a Cu/ZnO catalyst with the copper particles existing in both the Cu^0 and Cu^{1+} states. They found that on the Cu^0-rich catalyst surface only methoxy species were formed, but on a Cu^{1+}-rich surface formate was mostly produced. It is clear therefore that the interaction of methanol and oxygen in the presence of Cu is dependent on the nature of the oxygen species present. Here we present data complementing that of Harikumar and Rao, which compares their results to those we have obtained for methanol adsorption on bulk copper oxides using TPD.

2. Experimental

Experiments were carried out in a diffusion pumped stainless steel vacuum chamber with a base pressure of 2×10^{-10} mbar. XPS measurements used a VSW 100 mm radius hemispherical analyser and Al(K_α) photons. TPD was carried out by radiative heating of the sample from a tungsten filament heater situated close to the rear of the sample at a ramp rate of $\sim 3\ K\,s^{-1}$ and was monitored using a VG quadrupole mass spectrometer. Desorption peak maxima were reproducible to ±5 K. Dosing was carried out by backfilling the chamber to pressures of between 1×10^{-2} and 1×10^{-5} mbar with the sample at ∼300 K for 10 min. Gas exposures are quoted in langmuirs (L), where $1\ L = 1\ Torr\,s^{-1}$. The sample was pressed on to a stainless steel mesh with a chromel–alumel thermocouple attached, and this was mounted on an x-y-z rotational manipulator. The thermocouple is positioned in the centre on the sample area so that it is completely surrounded by the sample powder. The sample volume is relatively small and in particular very thin, only slightly thicker than the diameter of the wire mesh (wire diameter 0.25 mm, 40 × 40 wires/inch), so as to minimise uneven heating of the sample. The weight of the catalyst used was typically 0.2 g. The CuO and Cu_2O samples (Aldrich Chemical Co.) were bulk powders used as received, XRD and XPS analyses of these samples revealed no detectable impurities other than small amounts of carbon in XPS. Their surface areas were both measured at around $2\ m^2\,g^{-1}$. No impurities were detected in the methanol (Fisher Scientific 99.99%) and formic acid (Fisher Scientific >98%) vapour by mass spectrometry.

3. Results and discussion

XPS measurements were carried out on the samples in order to determine the surface composition of the copper oxide samples prior to dosing with formic acid or methanol. These results have been discussed in more detail elsewhere [42], but can be summarised as follows. Vacuum-annealing of Cu_2O at 770 K resulted in the formation of a thin surface film of Cu metal which we estimate to be a single atom thin. In the case of CuO, brief vacuum-annealing (10 min) at 773 K followed by heating in 1×10^{-4} O_2 at the same temperature produced a fully oxidised CuO surface. Prolonged vacuum-heating (8 h) at 800 K produced a thick film of Cu_2O with no apparent sign of the reduction of the surface to Cu metal encountered for the bulk Cu_2O sample.

3.1. *Formic acid adsorption on Cu oxides*

Figure 1 shows a TPD profile for formic acid adsorbed at 300 K on CuO vacuum-annealed to give a thick film of Cu_2O. Formic acid adsorption produces formate at 300 K, and so the main feature of the TPD was the coincident evolution of CO_2, H_2 and H_2O characteristic of formate decomposition (equations (1)–(3)), with some of the hydrogen atoms combining with lattice oxygen to produce water. The main CO_2 desorption peak occurred at 545 K though there was also a less intense desorption peak at 430 K.

$$\mathrm{HCOO(ad)} \rightarrow \mathrm{CO_2(g)} + \mathrm{H(ad)} \tag{1}$$

$$\mathrm{H(ad)} + \mathrm{H(ad)} \rightarrow \mathrm{H_2(g)} \tag{2}$$

$$\mathrm{2H(ad)} + \mathrm{O(ad)} \rightarrow \mathrm{H_2O(g)} \tag{3}$$

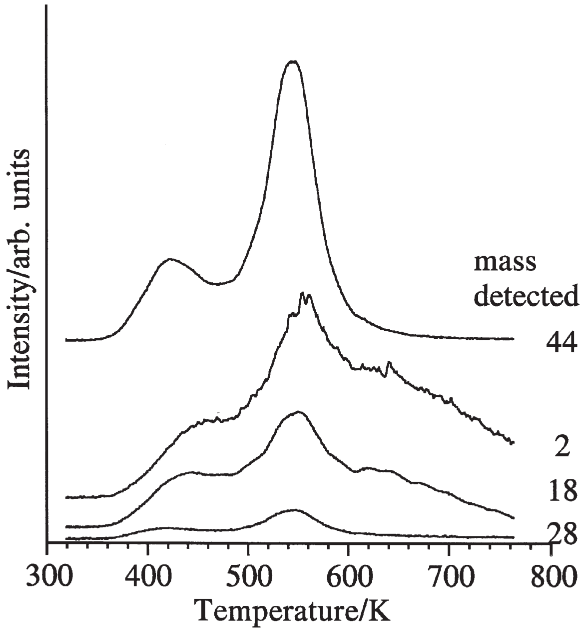

Figure 1. TPD following formic acid adsorption at 300 K (2×10^{-5} mbar, 10 min) on CuO vacuum-annealed to 800 K for 8 h. The masses detected are indicated on the right of the desorption profile with any scaling factor shown in brackets. The masses correspond to the following desorption products: H_2 mass 2, CO_2 mass 44, H_2O mass 18. The mass 28 signal can be accounted for as a cracking fragments of CO_2. The profiles are offset for clarity.

The formate decomposition peak at 550 K is at a very much higher temperature than is the case for formate on Cu(110) which occurs at 480 K [1]. An explanation for this can be obtained from INS experiments which we have recently conducted for formic acid adsorption on copper oxides [43,44]. They show that the adsorption of formic acid at 300 K on CuO, both fully oxidised and vacuum-annealed, produces an INS spectrum very similar to bulk copper(II) formate, more so in the case of the fully oxidised CuO. In particular, there is a close similarity in the low-frequency region where the lattice vibrations occur. The formate overlayer therefore appears to contain a degree of extended three-dimensional formate–Cu bonding which may greatly stabilise the overlayer when compared to a single bidentate formate adsorbed on Cu(110). We have performed a number of TPD experiments involving formic acid adsorption at 300 K on copper surfaces ranging from metallic copper to fully oxidised CuO, and there is a clear trend to higher formate decomposition temperature with increasing level of oxidation of the surface consistent with the transition from bidentate adsorbed formate to bulk-like copper(II) formate. The difference in the formate decomposition temperature with surface oxidation state can be illustrated with reference to figure 2. Figure 2 shows TPD profiles for formic acid adsorbed at 300 K on vacuum-annealed Cu_2O. Formic acid adsorption produces a main CO_2 desorption peak maximum at 485 K, a significantly lower temperature than for vacuum-annealed CuO (figure 1). There is again also a lower temperature desorption state at 375 K. The reason for two formate decomposition peaks in both figures 1 and 2 is not clear, but may originate from the presence of two formate species with different adsorption geometries, possibly monodentate and bidentate. The bidentate species would be expected to decompose at the higher temperature.

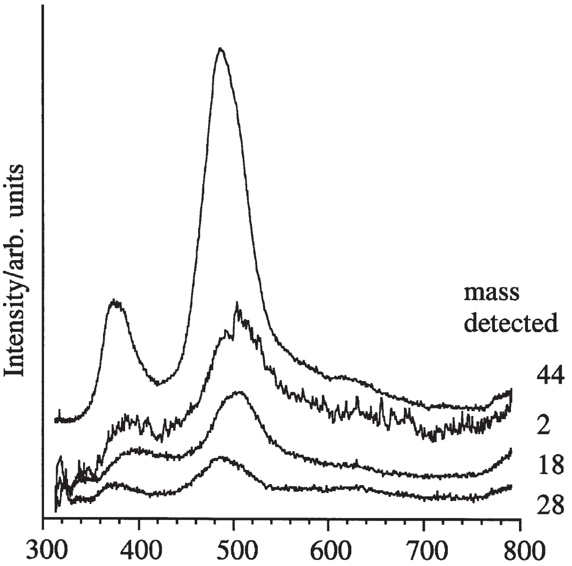

Figure 2. TPD following formic acid adsorption at 300 K (5×10^{-5} mbar, 10 min) on Cu_2O vacuum-annealed to 800 K. The profiles are offset for clarity.

3.2. Methanol adsorption on Cu oxides

Methanol adsorption was carried out on all three of the surfaces mentioned above, i.e., (a) vacuum-annealed Cu_2O, (b) CuO vacuum-annealed to give a thick Cu_2O film at the surface, and (c) CuO with a fully oxidised surface. In contrast to the case of formic acid adsorption, methanol exposures of up to 6×10^6 L (1×10^{-2} mbar for 10 min) on vacuum-annealed Cu_2O failed to produce any desorption products. This may at first seem surprising in comparison to the results of Harikumar and Rao [41], who found significant formate production for methanol adsorption on Cu^{1+} particles. However, the difference can be explained by reference to the XPS results [42] which show that our vacuum-annealed Cu_2O sample has a surface film of copper metal. It appears therefore that this behaviour is similar to that of bulk copper metal rather than Cu^{1+} in respect to methanol adsorption. It is known from surface science studies of methanol adsorption on Cu(110) that the sticking probability of methanol on clean Cu(110) at 300 K is very low (<0.03) [16], and that no adsorption occurs for exposures of at least several hundred langmuirs. However, on the oxygenated Cu(110) surface the sticking probability can be as high as 0.2 at 300 K which shows that the oxygenated surface is considerably more reactive towards methanol than Cu metal. Similarly Harikumar and Rao [41] found that, though methanol adsorption (and subsequent methoxy formation at 180 K) occurred on the Cu component of a Cu/ZnO/Zn model catalyst with methanol adsorption at 150 K, the methoxy totally decomposed by 300 K. The vacuum-annealed Cu_2O sample exhibited Cu metal-like reactivity toward CH_3OH, even though the Cu film thickness appears very low. However, there is support in the literature for very thin Cu metal films behaving like the bulk metal. Campbell and Ludviksson [45] found that atom-thin two-dimensional Cu islands on Zn(0001) react with HCOOH and CH_3OH very much like Cu(110).

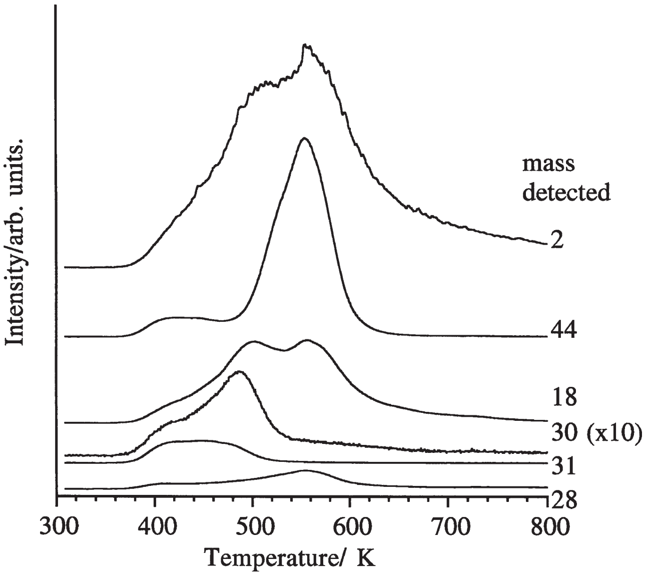

Figure 3. TPD following methanol adsorption at 300 K (1×10^{-4} mbar, 20 min) on CuO vacuum-annealed to 800 K for 8 h. The masses detected are indicated on the right of the desorption profile with any scaling factor shown in brackets. The masses correspond to the following desorption products: H_2 mass 2, CO_2 mass 44, H_2O mass 18, H_2CO mass 30, CH_3OH mass 31, CO mass 28. The mass 28 and 30 signals also contain a contribution from the cracking fragments of CO_2 and CH_3OH, respectively. The profiles are offset for clarity.

Figure 3 shows TPD data for methanol adsorbed at 300 K on CuO after it has been vacuum-annealed to produce a thick surface film of Cu_2O. In this case, methanol did adsorb with desorption products being detected. The desorption profiles were dominated by peaks from CO_2, H_2 and H_2O which were all desorbed coincidently at 555 K, though the H_2O and H_2 peaks were significantly broader than the CO_2. The coincident desorption of CO_2, H_2 and H_2O are characteristic of formate decomposition, as shown in equations (1)–(3), with some of the hydrogen atoms combining with lattice oxygen to produce water. The broadness of the 2 and 18 signals may be due to recombinative desorption from hydroxyl groups formed on the surface by the deprotonation of the methanol on adsorption (equation (5)). In addition, in figure 3 there is a group of lower-temperature desorption peaks between 350 and 500 K indicating the desorption of methanol and formaldehyde together with more extensive oxidation products CO_2 and H_2O. The CO_2 and H_2O probably arise from formate decomposition. As shown in figures 1 and 2 above, formate decomposition produces a minor set of CO_2, H_2 and H_2O desorption peaks in this temperature range. The mass 30 signal (formaldehyde) represents only ~5% of the 44 (CO_2) peak area, and the mass 31 signal (CH_3OH) represents ~10% of the CO_2 signal. Formaldehyde is formed from the decomposition of methoxy (equation (4)) and is the main decomposition pathway for methoxy when it is produced by adsorbing methanol on oxygen-precovered Cu(110) [16]. TPD data for methanol adsorbed on a fully oxidised CuO surface are shown in figure 4 and, again, show that the main desorption products are CO_2, H_2 and H_2O, though the CO_2 desorption maximum was shifted to 570 K compared with 555 K in figure 3. Again, these data show that the major stable surface species that produces desorption products is formate produced by oxidation of the methanol (equations (5)–(7)). As expected from the formic acid adsorption data presented above, formate decomposition from the more oxidised CuO surface (figure 4) occurs at slightly higher temperature than for the vacuum-annealed CuO surface shown in figure 3. Only the CO_2, H_2 and H_2O signals are shown, though formaldehyde and methanol were also desorbed with a peak maximum at 505 and 460 K and with a considerably lower intensity relative to CO_2 than in figure 3 at 0.2% of the CO_2 signal for formaldehyde and 1% for methanol. The more oxidised surface is, therefore, less selective for formaldehyde production as expected [27]. Another effect which we observed on comparing the methanol TPD profiles from the two surfaces is an alteration in the relative ratios of $CO_2 : H_2 : H_2O$. The H_2/CO_2 ratio in figure 4 is $\sim 1/3$ of the value in figure 3, that is, there is less H_2 relative to CO_2 for desorption from the fully oxidised CuO surface.

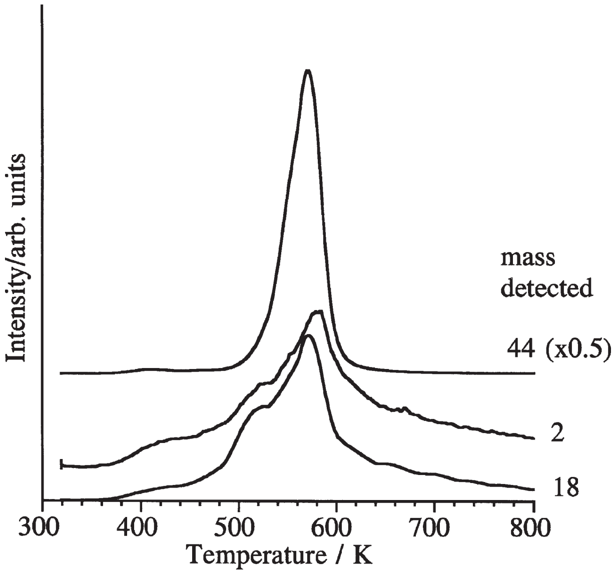

Figure 4. TPD following methanol adsorption at 300 K (1×10^{-4} mbar, 20 min) on fully oxidised CuO. The surface was prepared by heating CuO powder to 773 K for 15 min in 1×10^{-4} mbar oxygen and checked with XPS in order to confirm the surface was fully oxidised to CuO. The profiles are offset for clarity.

Conversely, the H_2O/H_2 ratio in figure 4 is four times larger than in figure 3, showing that there is more H_2O desorption relative to H_2 from the fully oxidised CuO surface. The more oxidised surface (figure 4) is, therefore, more efficient at converting the hydrogen, produced on formate decomposition, to water.

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

$$CH_3OH(g) \rightarrow CH_3OH(ad) \tag{5}$$

$$CH_3OH(ad) + O(ad) \rightarrow CH_3O(ad) + OH(ad) \tag{6}$$

$$CH_3O(ad) + 3O(ad) \rightarrow HCOO(ad) + 2OH(ad) \tag{7}$$

It is clear from the TPD data that on the vacuum-annealed and fully oxidised CuO surfaces most of the adsorbed methanol is being converted to formate. This is consistent with the observation by Harikumar and Rao [41] that formate is the predominant surface species after adsorption of methanol on Cu clusters deposited on ZnO/Zn when the Cu has been oxidised to form Cu^{1+} species.

From the TPD data alone it would be difficult to distinguish between formate production at room temperature upon methanol adsorption, or whether the formate is produced during the TPD experiment at some elevated temperature. In this respect, it is useful to compare these data with those of Harikumar and Rao [41], who use XPS to observe the production of formate at or just below room temperature. This would suggest that in our experiments, the formate is in fact produced at 300 K. It is also of interest to note that recent STM experiments which we have performed [34–37] indicate the production of formate during co-dosing of methanol and oxygen on Cu(110) at 300 K. Others have also reported the production of formate following sequential dosing of oxygen then methanol at 300 K [32,33,38,39].

There is a close similarity of the main formate decomposition peak temperature when formic acid is adsorbed, and when methanol is adsorbed, which shows that in the case of methanol adsorption, the decomposition of the formate is not determined by the temperature at which formate is produced, but by the temperature at which the formate decomposes.

4. Conclusions

Methanol adsorption on vacuum-annealed CuO and fully oxidised CuO surfaces results predominantly in the production of formate which decomposes to H_2, CO_2 and H_2O in TPD experiments. No significant amounts of desorption products were observed following methanol adsorption on vacuum-annealed Cu_2O at 300 K. This lower reactivity is attributable to the reduction of the surface to copper metal on vacuum-annealing. The main formate decomposition peak maximum following methanol adsorption on the CuO surfaces occurred at 555–570 K, very similar to the decomposition temperature of formate produced by formic acid adsorption on these surfaces.

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