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The chemisorption of methanol on Cu films on ZnO(000$\bar{1}$)-O

R. Zhang, A. Ludviksson and Charles T. Campbell

Department of Chemistry, BG-10, University of Washington, Seattle, WA 98195, USA

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The interactions of methanol with well-defined Cu films on the oxygen-terminated ZnO(000$\bar{1}$)-O surface have been studied, mainly using temperature programmed desorption (TPD). The Cu films, which were from submonolayer to multilayer in coverage, had been structurally characterized in previous studies using XPS, LEIS, ARXPS, LEED and work function measurements, and by CO, H_2O and formic acid adsorption. On clean Cu films methanol is adsorbed reversibly, desorbing at 200–260 K from atom-thick Cu islands, and at ~ 155 K from multilayer islands preannealed to ~ 550 K. In this respect, the atom-thin islands resemble Cu(110) sites and multilayer islands resemble Cu(111), consistent with behavior of other adsorbates. On oxygen-predosed multilayer films (preannealed to ~ 600 K), methanol reacts to form methoxy species which decompose at 395 K to yield formaldehyde and hydrogen in TPD, also like Cu(111). Multilayer films preannealed to >750 K show a decrease in the peak area for methoxy decomposition which correlates with the loss of Cu area due to severe clustering. Oxygen-predosed Cu islands which are but one Cu atom thick show no clear evidence for a methoxy state in TPD. This suggests that oxygen atoms on such atom-thin Cu islands are poor Brønsted bases relative to O_a on bulk Cu surfaces, consistent with results for adsorbed water. Results on high-area Cu/ZnO catalysts are discussed in the light of these new results.

Keywords: Cu/ZnO catalysts; methanol synthesis catalysts; model catalysts based on single crystals; metal–support interactions; surface chemistry of Cu/ZnO; methanol adsorption

1. Introduction

Cu/ZnO catalysts are used industrially for the water–gas shift reaction, methanol steam reforming and methanol synthesis. Therefore, the interaction of methanol with such catalysts is of significant interest. Due to the complexity and heterogeneity of a real catalyst surface, the exact role and form of the individual components in the catalyst has not been evaluated unequivocally (refs. [1–5], and references therein). The adsorption and surface reactions of methanol with high-surface area Cu/ZnO catalyst has been previously studied [6–8]. The results are rather complex, and it is difficult to associate spectral features with distinct sites on the surface.

In order to simplify the very heterogeneous environment found on the surface of a real catalyst for fundamental study, several studies of methanol adsorption have been performed on pure, single-crystalline samples which present one site probably present on the real catalyst. For example, the interactions of methanol with single crystal Cu surfaces have been well studied [9–16], as have different surfaces of ZnO single crystals [17–23]. Methanol desorbs below 300 K from ZnO(000$\bar{1}$)-O, with no evidence of dissociation [22,23]. Methanol desorbs well below room temperature from clean Cu (111), (100) and (110), with perhaps a tiny amount of decomposition [9–16]. If oxygen is predosed to these Cu crystals, methanol decomposition is very efficient, via [9–16]

$$CH_3OH_a + O_a \rightarrow CH_3O_a + OH_a\,. \tag{1}$$

The resulting hydroxyls disproportionate below 300 K to release water in TPD. The surface methoxy decomposes at ~ 365–385 K via

$$CH_3O_a \rightarrow H_2CO_g + H_a\,. \tag{2}$$

The H_a product of this step mostly desorbs immediately as H_2. A small amount reacts with other methoxys to produce methanol gas [9–16].

In a related study addressing possible synergistic interactions between the Cu and ZnO phases, Fu and Somorjai [24] prepared three-dimensional ZnO_x islands on a Cu(110) surface. This ZnO_x film dissociated methanol efficiently, producing TPD peaks for methoxy decomposition ($CH_2O + \frac{1}{2}H_2$) at 340–540 K and for formate decomposition at 540 K ($CO_2 + H_2O$) and at 580 K ($CO + H_2$). In addition, they observed the peaks expected from the ZnO_x-free Cu(110) regions of the surface described above.

Here we report a study of adsorption and surface reactions of methanol on vapor-deposited Cu films grown on the oxygen-terminated ZnO(000$\bar{1}$)-O surface. This approach generates a model catalyst that closely resembles the local microstructure of real Cu/ZnO catalysts, which are known to be mainly composed of tiny metallic Cu islands supported on ZnO particles [25–30]. We [31–35] and others [36] have prepared and characterized vapor-deposited thin films of Cu on this surface of ZnO. In our recent studies using XPS, LEIS, ARXPS, LEED and work function measurements, it was found that submonolayer Cu films form 2D metallic islands which are but one atom (2.2–2.6 Å) thick and can cover up to 55% of the ZnO when deposited to a cold substrate [31–34]. This submonolayer Cu adsorbs CO, H_2O and HCOOH much like the Cu(110) surface of bulk Cu [32–34]. Higher Cu coverages grow 3D metallic clusters with many low-coordination Cu atoms at the surface, having large portions of the ZnO free of Cu. Annealing these films to > 550 K increases the number of clean ZnO sites, increases the thickness of the Cu clusters slightly, and converts most of their surfaces to Cu(111)-like sites [31–34]. Annealing above ~ 750 K causes severe loss of Cu area, attributed to severe three-dimensional clustering [31–34]. We report here chemisorption and reaction studies of methanol on Cu overlayers on ZnO(000$\bar{1}$)-O wherein the Cu islands are both a two-dimensional (i.e., one atom thick) and three-dimensional (more than several atoms thick), and with these same Cu overlayers after they have been exposed to oxygen gas to generate surface oxygen.

2. Experimental

The experiments were performed in an ultrahigh vacuum (UHV) apparatus described previously [31], with a base pressure of 10^{-10} Torr. It had capabilities for X-ray photoelectron spectroscopy (XPS), LEED, low-energy He^+ ion scattering spectroscopy (LEIS), and temperature programmed desorption spectroscopy (TPD) using a quadrupole mass spectrometer interfaced to a computer for multiplexing masses. All XPS spectra reported here use Al K_α radiation (1486.6 eV).

The preparation, mounting, and cleaning procedures for the ZnO sample used in this study are described elsewhere [31], as are the control experiments we performed to ensure that our thermocouple was truly monitoring the sample temperature during TPD. Heating rates for TPD were about 5 K/s. Copper was vapor deposited as described previously [31]. Dose rates were found to be reproducible to better than 10% from day to day, judging by XPS signals. The coverages we quote here for Cu were determined from the Cu(2p)/Zn(2p) XPS ratio measured immediately after deposition of Cu onto ZnO at 125 K. This ratio was converted into absolute coverage units using the calibration of ref. [31], performed in this same instrument. Research-grade methanol and O_2 were used in this study. Methanol was purified by several cycles of freezing in liquid nitrogen followed by evacuation and then thawing. The purity of methanol and O_2 were routinely verified to be better than 99% in the vacuum chamber using a mass spectrometer. The dosing of methanol was accomplished using a pinhole cosine source located about 1.5 cm from the sample. Methanol exposures here are reported in "dosing units", which correspond to 0.05–0.1 L (langmuir).

3. Results and discussion

3.1. METHANOL DESORPTION FROM CLEAN ZnO(000$\bar{1}$)-O

Except for an early study of ZnO single crystals [19], which found comparable extents of decomposition of adsorbed oxygenates on the (000$\bar{1}$)-Zn and (000$\bar{1}$)-O polar faces, it is generally accepted that (000$\bar{1}$)-O surface is non-reactive due to the absence of accessible acid–base site pairs necessary for dissociative adsorption on this surface [22,23]. In this present study, no dissociative adsorption of methanol was found on clean ZnO(000$\bar{1}$)-O surface. We extended our study to low temperature to probe the molecular desorption states of methanol, which have also been previously studied by Zwicker et al. [22]. The TPD spectra for methanol on clean ZnO(000$\bar{1}$)-O for different exposures at 125 K are shown in fig. 1. There are two adsorption states even at very low exposures, with TPD peak temperatures of about 190 and 230 K. Both peaks shift by ~ 30–40 K (~ 16%) to lower temperature with increasing exposure. At about 12 dosing units, these peaks saturate, and another low temperature peak begins to grow. This peak does not saturate, and at

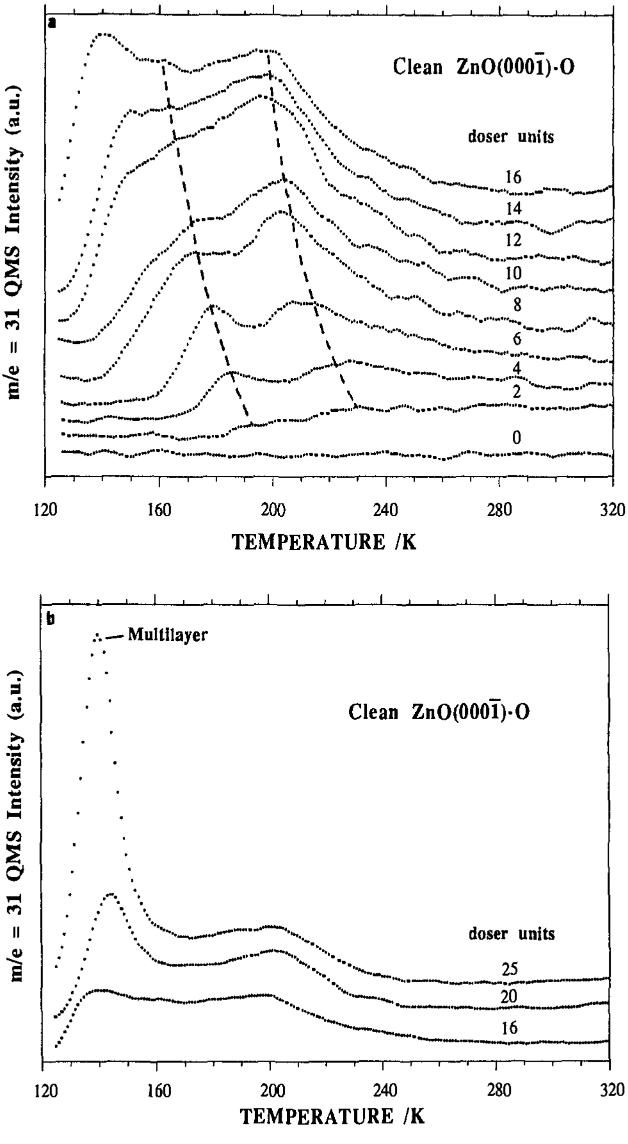

Fig. 1. Molecular methanol TPD spectra following methanol adsorption on clean ZnO(000$\bar{1}$)-O at 125 K. (a) Low exposures, and (b) high exposures. Heating rate was ~ 5 K/s.

about 25 dosing units, it reaches its lowest peak temperature of ~ 140 K. Beyond 25 dosing units (spectra not shown), this peak's temperature shifted up, indicative of multilayer desorption. This was confirmed by leading-edge analysis. The peak temperature for multilayer desorption at 140 K is consistent with previous studies of multilayer desorption of methanol from Cu(110) [12] and Ag(110) [37] surfaces. It is 20 K higher than reported by Zwicker et al. [22] from the ZnO(000$\bar{1}$)-Zn surface. Zwicker et al. [22] also described TPD spectra for adsorbed methanol on the ZnO(000$\bar{1}$)-O surface that are very similar to those presented in fig. 1, except that our spectral features were shifted uniformly by ~ 20 K to higher temperature, suggesting a possible thermocouple contact problem in ref. [22].

The higher-temperature peaks will be assigned to: (a) methanol bound to oxygen anion sites of the ZnO, desorbing at 200–300 K, and (b) methanol bound in a weaker state, perhaps in a second layer, desorbing at 160–190 K. The fact that these peaks populate simultaneously indicates that the second state begins to populate before the first one is saturated. The shifts in these peaks with coverage to lower temperature indicates that there are strong dipole repulsions between the adsorbed methanol molecules in both states. It can be expected that this kind of lateral interaction would be stronger on a semiconductor surface than on a metal surface, since there are fewer conduction electrons to screen the electric field.

3.2. METHANOL DESORPTION FROM 3D AND 2D Cu ISLANDS

Fig. 2 shows TPD of methanol from a Cu film of coverage 10 N_1 (1 N_1 corresponds to about 1.1×10^{15} atoms/cm^2 [31]), for increasing methanol exposures. These Cu films had been flashed to 500 K prior to methanol adsorption. It is obvious that, similar to methanol desorption from clean ZnO(000$\bar{1}$)-O, the second peak begins to appear before the first one is completed. Finally at about 25 doser units, the multilayer desorption peak appears at 140 K. When desorption spectra from this figure are directly compared to spectra from fig. 1 for the same methanol coverage (i.e., same integrated TPD area) on clean ZnO, it is obvious that there is more intensity in the range 150–160 K and less in the range 190–260 K on the Cu dosed surface. The new intensity around 155 K is attributed to methanol on Cu sites, and the lost intensity is attributed to ZnO sites masked by the Cu film. The overlapping regions, which account for most of the intensity, are due to ZnO sites that are not masked by Cu and accidental similarities in the desorption regions for Cu and ZnO sites.

Methanol shows a dominant monolayer desorption peak at 153 K from Cu(111) [38], close to the peak at 155 K we attribute here to Cu sites. In contrast, Cu(110) shows its methanol monolayer TPD peak at 195 K, with a strong shoulder at 265 K [10,13,24]. This comparison shows that the surfaces of these thick, annealed Cu islands on ZnO more closely resemble Cu(111) sites than Cu(110) sites with respect to their chemisorption of methanol. This conclusion is consistent

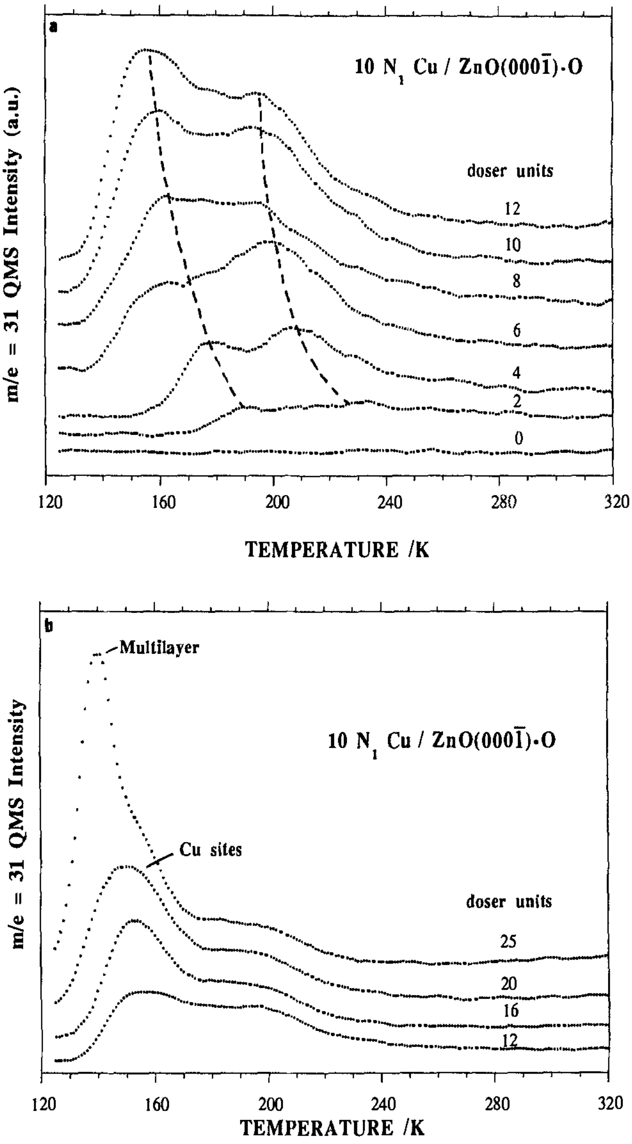

Fig. 2. Molecular methanol TPD spectra following methanol adsorption on a ZnO(000$\bar{1}$)-O surface containing 3D Cu islands at 125 K. (a) Low exposures, and (b) high exposures. (In all spectra, the Cu coverage was 10 N_1, flashed to 500 K before methanol adsorption.)

with LEED and ARXPS results which show the islands to assume Cu(111) structure [31] and with TPD spectra for other molecules [32–34].

Similar experiments to those shown in fig. 2 were also performed on submonolayer Cu films of coverage 1 N_1 that were freshly-deposited at 125 K. Prior results [31] showed that such films are composed of Cu islands that are only one atom thick and cover ~ 50% of the ZnO. We refer to these as 2D Cu islands. The differences between the TPD spectra of methanol from ZnO with and without this 2D Cu are even smaller than the differences mentioned above for 3D Cu islands. Thus, methanol desorption kinetics from 2D Cu is very similar to that from clean ZnO(000$\bar{1}$)-O. The only significant difference between 2D Cu on ZnO and the clean ZnO spectra for the same TPD peak areas was a slight increase in desorption intensity in the broad region from 200 to 260 K, at the expense of intensity at the leading edge. We attribute the increased intensity at 200–260 K to 2D Cu sites. Comparing to the TPD temperatures mentioned above for methanol from Cu (111) and (110), this intensity at 200–260 K shows that these 2D Cu islands offer sites that resemble Cu(110) sites, and not Cu(111) sites. This has been observed in the chemisorption of other species on these Cu films [32–34], and can be attributed to the more corrugated nature of the Cu surface for 2D islands, and / or electronic effects of the underlying oxygen anion layer.

The 3D Cu films showed, on the average, a somewhat increased TPD peak area for the same methanol exposure when compared to clean ZnO. The extent of increase indicated that the sticking probability for methanol at 125 K increased by ~ 40% for 3D films.

There was no evidence for dissociation in the TPD spectrum of methanol on the 3D Cu film without oxygen pretreatment, also consistent with results on Cu(111) [38], and on Cu(100) [39]. The 2D Cu film also showed no significant methanol decomposition without oxygen pretreatment. The clean Cu(110) surface shows measurable methanol decomposition during TPD, but only to a small extent (a few percent of a monolayer) [9–13]. In contrast, oxygen-predosed Cu single crystals show very high reactivity for the decomposition of methanol during TPD [9–13] (see section 1 also).

3.3. METHANOL AND METHOXY DECOMPOSITION ON OXYGEN-PREDOSED Cu FILMS

Oxygen-predosed 3D Cu films on ZnO similarly show strong TPD peaks for methoxy decomposition following methanol adsorption, whereas no decomposition is seen without oxygen. For comparison, fig. 3 shows TPD spectra of mass signals 2, 29 and 31 following methanol adsorption at 125 K on Cu/ZnO(000$\bar{1}$)-O, with and without O_2 pre-dose. Here, the Cu coverage of 10 N_1 had been preannealed to 600 K before exposure to O_2 or methanol. The O_2 exposure (2 L) was dosed at 125 K, then flashed to 300 K briefly to ensure that the O_2 was in dissociated form on the surface. This oxygen exposure was chosen to maximize the amount of methanol decomposition, based on previous studies of the oxygen dependence of methanol decomposition on Cu(110) [9,10] and Cu(111) [15]. No detailed study about the surface oxygen coverage dependence of methoxide peak intensity was done in the present work. The methanol exposure of 25 doser units was given to the surface at 125 K. Without O_2 pre-treatment, there is almost no desorption beyond 300 K. Only trace amounts of mass 29 signal are detected at

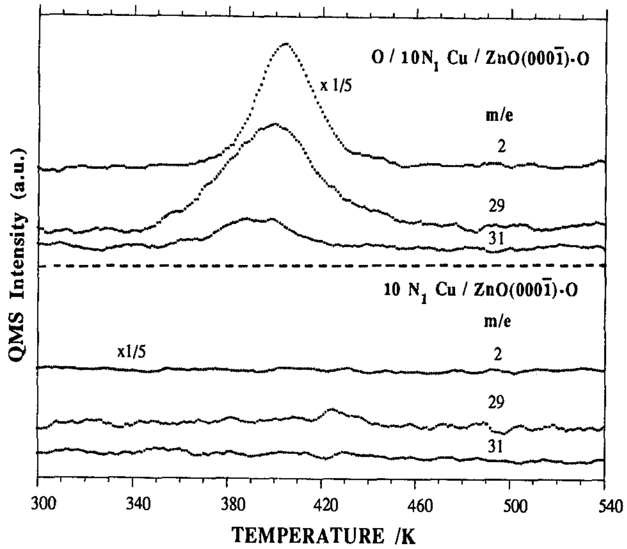

Fig. 3. Comparison of TPD spectra showing methoxy decomposition region at $m/e = 29$ (formaldehyde) and $m/e = 31$ (methanol) following methanol adsorption on Cu/ZnO(000$\bar{1}$)-O with and without O_2 treatment. The Cu coverage here was 10 N_1, flashed to 600 K before oxygen treatment. The O_2 exposure of 2 L at 125 K was briefly flashed to 300 K before "saturation" methanol exposure at 125 K. By "saturation" exposure here we mean ~ 20 doser units, which is enough to saturate the decomposition peaks and the molecular desorption peaks associated with Cu or ZnO sites in TPD, and to just begin populating the multilayer TPD peak.

430 K, which might be caused either by a trace amount of formaldehyde in the methanol or by a small amount of O_2 adsorbed from the residue gas during the Cu deposition process. If predosed with O_2, strong peaks for H_2 ($m/e = 2$) and formaldehyde (H_2CO, $m/e = 29$) are observed nearly simultaneously at ~ 400 K, as shown in fig. 3. These peaks can be attributed to the decomposition of methoxy according to reaction (2) above. The methoxy is then assumed to have been formed below 300 K via reaction (1) above, as on bulk Cu surfaces. A peak at $m/e = 31$ due to methanol is also seen at ~ 400 K. It is of about the same magnitude as seen from bulk Cu samples [9,10,15], and will be attributed to the same process as reported there [9,10,15],

$$CH_3O_a + H_a \rightarrow CH_3OH_g . \qquad (3)$$

The hydrogen used in this step resulted as a product of reaction (2), which explains why this methanol peak is simultaneous with H_2 and formaldehyde desorption.

Curiously, no TPD peaks were seen in these experiments for H_2 or H_2O that could be associated with removal from the surface of the acid hydrogen of methanol. This hydrogen is transferred to the surface in producing the methoxy species according to reaction (2). We attribute this to the fact that this hydrogen diffuses rapidly off of the Cu islands and into the near bulk of the ZnO. This same disappearance of the acid hydrogen also occurred in TPD of formic acid from these Cu/

ZnO films, as was proven by isotopic tracing and nuclear analysis of the near bulk composition [34].

No TPD peaks due to formate decomposition were ever observed for these Cu/ZnO films following methanol adsorption, with or without oxygen predose. This proves that formate is not produced in significant amounts during TPD of methanol, since such formate decomposition peaks are easily identified and measured in TPD from these same Cu/ZnO films when the formate is instead produced by formic acid decomposition [34].

The TPD spectra following methanol adsorption on pre-oxidized Cu films on ZnO(000$\bar{1}$)-O at different Cu coverage are shown in fig. 4 for mass signal 29 (H_2CO) and mass signal 2 (H_2). The Cu, oxygen and methanol doses and annealing sequences were the same as described for fig. 3, except that different amounts of Cu were used. It is obvious that the formaldehyde ($m/e = 29$) peak at ~ 400 K due to methoxide decomposition is absent for Cu coverages up to 1 N_1, increases dramatically with the Cu coverage between 1 N_1 and 2 N_1, and then grows more slowly above 2 N_1. Saturation is slowly approached above 4 N_1. The peak areas for both this peak and the corresponding $m/e = 2$ (H_2) peak are plotted versus Cu coverage in fig. 5. The strongly nonlinear behavior seen at $m/e = 29$ below 2 N_1 is also seen at $m/e = 2$, but it is somewhat weaker for the latter. The noise is worse also in the latter, so the error bars on the areas are worse. The shape of the $m/e = 2$ curve is also undoubtedly perturbed by competition from hydrogen diffusion into and out of the bulk of the ZnO from these Cu films, as was also the case in our studies with formic acid [34]. The shape of the formaldehyde curve in fig. 5 to a large extent merely reflects the Cu surface area before annealing, as measured previously by LEIS [31] an CO chemisorption [32]. However a major difference between this curve and the Cu surface area exists at the Cu coverage 1 N_1, since the Cu surface area at this point is nearly as large as the Cu area at 2 N_1 [31,32]. (Annealing should not change this much [31,32].) The Cu islands at coverage 1 N_1 are only one atom thick, whereas they are two atoms thick, on average, at 2 N_1 [31]. This is similar to results from our H_2O adsorption study on these same Cu films [33]: at 1 N_1, no hydroxyl groups were formed when H_2O was dosed onto the preoxidized Cu film, whereas preoxidized, bulk Cu surfaces would readily have dissociated the water under these conditions according to the analogous reaction to (1) above:

$$H_2O_a + O_a \rightarrow 2OH_a . \qquad (4)$$

The absence of reactions (1) and (4) at a Cu coverage of 1 N_1 strongly suggests that O_a on these Cu islands is not as efficient at hydrogen abstraction as is O_a on bulk Cu or on thicker Cu islands. That is, O_a is a much weaker Brønsted base on these atom-thin Cu islands.

Returning to fig. 4, the peak temperature for formaldehyde desorption shifted from ~ 408 K at Cu coverage of 2 N_1 to 395 K at 10 N_1. The hydrogen desorption peak temperature was uniformly ~ 10 K higher than the formaldehyde peak, and somewhat narrower. The higher temperature of the H_2 peak is attributed to the resi-

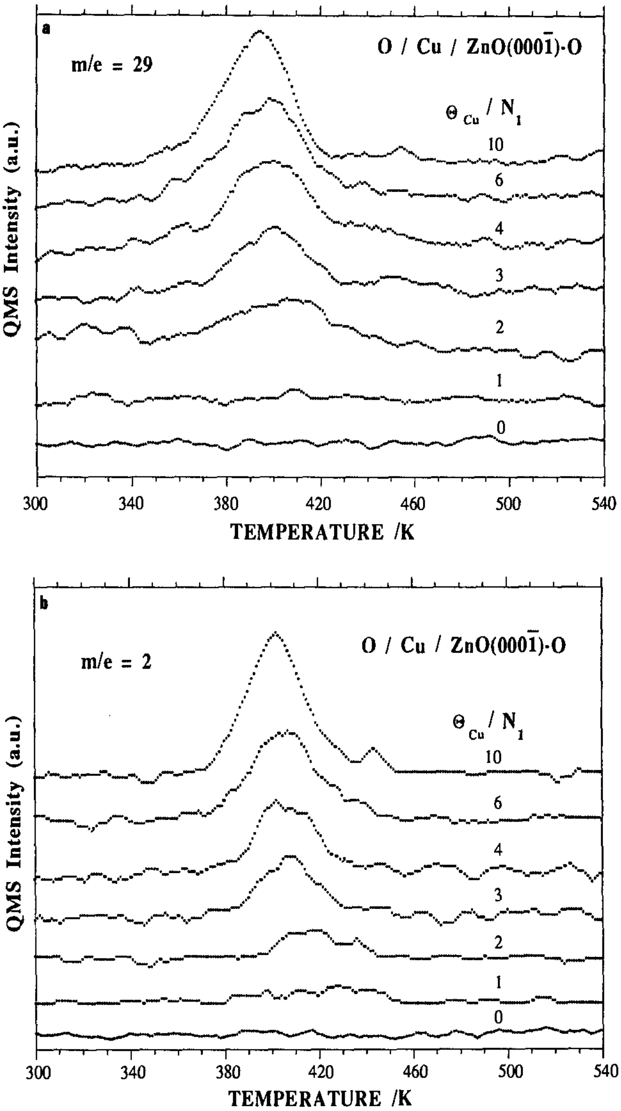

Fig. 4. TPD spectra showing methoxy decomposition following methanol adsorption on O_2-predosed Cu/ZnO(000$\bar{1}$)-O at different Cu coverages. (a) for mass 29 signals (formaldehyde); and, (b) for mass 2 signals (H_2). All these Cu films were dosed at 125 K, then briefly flashed to 600 K prior to an O_2 exposure of 2 L at 125 K. The surfaces were then flashed briefly to 300 K, and finally given a saturation methanol exposure at 125 K.

dence time of H atoms on the surface before desorption as H_2. This effect is also seen in TPD from bulk Cu surfaces [9,10,13]. The competing diffusion of H into and out of the bulk of the ZnO mentioned above certainly also influences the hydrogen lineshapes here. The formaldehyde peak temperature of 395 K at 10 N_1 is very close to the value of ~ 385 K reported for oxygen-dosed Cu(111) [15]. On the

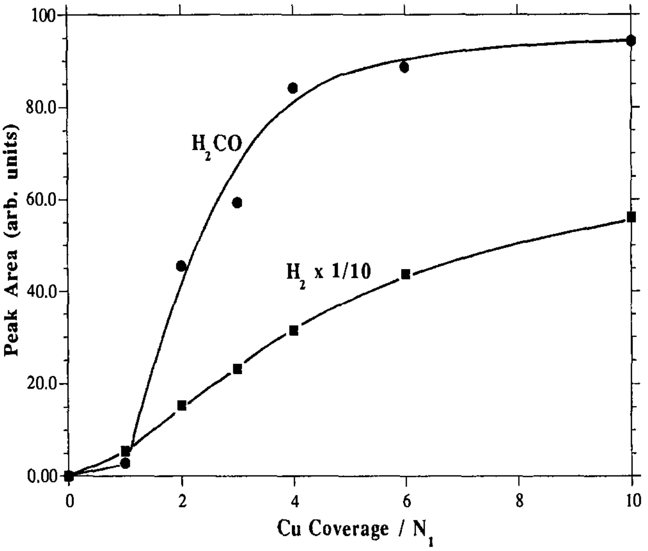

Fig. 5. TPD peak areas for methoxy decomposition versus Cu coverage on O_2-predosed Cu/ ZnO(000$\bar{1}$)-O. The data and experimental conditions are the same as given in fig. 4 above.

other hand it is significantly above the values of 365–375 K reported for O/ Cu(110) [9,10,13,24]. Again, this is consistent with the fact that these annealed, multilayer Cu islands have Cu(111)-like surface structure (see above). The thinner Cu islands (at 2 N_1) have a significantly higher formaldehyde peak temperature (408 K) than either Cu(111) or Cu(110). Since the formaldehyde peak is known to be rate-limited by C–H bond cleavage in the surface methoxy intermediate, the activation energy for this step must be 5–10% higher on these ultrathin Cu islands than on bulk Cu surfaces. This would suggest that the Cu atoms in these islands are less efficient at hydrogen abstraction. Consistent with this qualitative behavior are the peak temperatures for formate decomposition on these same Cu films [34].

3.4. ANNEALING EFFECTS ON THE Cu FILMS

Fig. 6 shows the influence of annealing the freshly-deposited Cu film of coverage 10 N_1 upon the formaldehyde ($m/e = 29$) TPD peak following methanol exposure. The Cu film was first deposited on the clean ZnO at 125 K, briefly (~ 1 s) annealed to the designated temperature, then pretreated with 2 L of O_2 at 150 K and finally flashed to 300 K before exposure to 25 doser units of methanol at 125 K. The H_2CO peak area in fig. 6, which reflects the total amount of methoxy decomposition, stays relatively constant until annealing to above 800 K, but it decreases rapidly above 800 K, so that the peak disappears into the background by 900 K. This peak area decrease is associated with the loss of Cu surface area, which has been shown to occur after annealing these Cu films by LEIS [31] and by CO

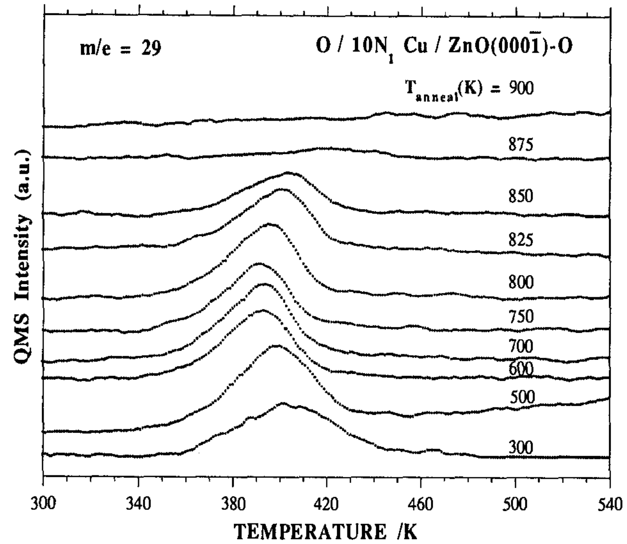

Fig. 6. TPD spectra showing the H_2CO desorption peak due to methoxy decomposition following methanol adsorption onto O_2-predosed Cu/ZnO(000$\bar{1}$)-O, presented as a function of annealing temperature. The Cu film, of coverage 10 N_1, was dosed at 125 K and briefly annealed to T_{anneal} prior to oxygen treatment. The O_2 exposure of 2 L at 125 K was briefly flashed to 300 K prior to the saturation methanol exposure at 125 K.

and water chemisorption capacity [32,33]. The loss in Cu surface area is attributed to clustering of thin, flat islands into thicker islands that cover less of the ZnO [31]. It begins already by 400 K when measured by LEIS [31]; and water adsorption on Cu sites shows a marked decrease by 700 K [33]. The amount of methoxy measured here, and the CO adsorption capacity measured in ref. [32], only decrease at higher temperatures. In the case of CO adsorption, it was postulated that this difference may be due to chemisorption – induced redispersion of the Cu clusters [31,32]. The thermodynamic driving force for this redispersion was explained to be the CO adsorption energy [31]. In the present case, it could come from the oxygen, methanol and/or methoxy adsorption energies. Since the first and last of these are larger than the CO adsorption energy, the driving force for redispersion here is even more favorable than in the case of CO.

The TPD peak profile and position in fig. 6 also change with the annealing temperature. The peak temperature starts at around 405 K for the unannealed film, shifts down to ~ 393 K when annealed to 600–750 K, then goes back up to 403 K after annealed to 850 K. The peak temperature in the annealing range 600–750 K is very close to the value of 385 K reported for Cu(111) [15], as mentioned above. This is consistent with the Cu(111)-like surface structure known to be present on these Cu islands when annealed to this temperature range [31–33]. We currently have no explanation for the higher TPD peak temperature seen for the films that were annealed to lower and higher temperatures than this 600–750 K range. A considerably lower peak temperature is seen on the rougher Cu(110) surface (see above). This peak is known to vary by ~ 20 K with coverage on Cu(110) [9], possibly due to dipolar adsorbate–adsorbate interactions. These would depend upon the metal micromorphology, which is known to change upon annealing above 350 K [31].

4. Comparison to Cu/ZnO catalyst

The adsorption and surface reactions of methanol on high-surface-area Cu/ZnO catalysts, with or without other supports, have been studied by several groups using vibrational spectroscopy [6–8]. They generally conclude that methanol adsorbs dissociatively to form methanoxy, hydroxyl and formate species. Millar, Rochester and Waugh [7] found that methanol exposure to a reduced Cu/ZnO/SiO_2 catalyst at 295 K produced methoxy species on both Cu and ZnO sites, and a bridging formate species on Cu sites. After heating this surface to 393 K, the methoxy species on Cu sites disappeared, and formate species on Cu and ZnO sites became more apparent. With reduced Cu/ZnO catalysts, Edwards et al. [6] found that methanol dosing at 403–463 K produced methoxy, hydroxyl and formate species, all assigned to ZnO sites. Neophytides et al. [8] studied a Cu/ZnO/Al_2O_3 catalyst and found that methanol adsorption produced peaks for methoxy species (assigned to ZnO sites) and formate (shown to be at Cu sites). Upon heating at 0.17 K/s, the methoxy species disappeared at 413 K, with simultaneous evolution of formaldehyde and methanol into the gas phase; whereas the formate species disappeared at 463 K, with simultaneous evolution of CO_2 and H_2 in a 2 : 1 ratio. The TPD after methanol adsorption onto a very similar catalyst reported by Bowker et al. [5] has similarities, but at the same time considerable differences. The simultaneous methanol/formaldehyde peak was at ~ 370 K instead of 413 K, and it was accompanied by H_2, not seen in ref. [8]. There was a CO_2/H_2 peak at ~ 450 K, close to the 463 K value of ref. [8], but these species also showed a second peak, accompanied by CO, at ~ 610 K, unlike the results of Neophytides et al. [8].

These results bring up three significant questions when compared to our present results: (1) Why do we see no evidence for ZnO-bound species here? (2) Why is formate not produced on the Cu sites here? (3) Can our present results help clarify any of the infrared assignments? The first of these questions could easily be due to the fact that our oxygen-terminated ZnO surface offers no Zn^{2+} sites, except the few at defects. It is well known that this oxygen-terminated plane is the least reactive in chemisorption of all the ZnO surfaces [22,23]. Bonding to the Zn^{2+} cations may be necessary to create the species assigned to ZnO-sites in those vibrational spectra above. It is also possible that some of the assignments are not correct. Particularly questionable is the assignment of the methoxy species, which decomposes at 413 K with simultaneous evolution of formaldehyde and methanol, to binding at ZnO sites [8]. This decomposition temperature and its products are very similar to those seen for methoxy on Cu sites both here on 3D Cu islands (see above) and on Cu single crystals [9–16]. In contrast, these in no way resemble the behaviour of methoxy on the ZnO sites of ZnO single crystals [17–23]. We therefore suggest that the peaks for this species, which were at 1050, 2820 and 2935 cm^{-1} [8], be reassigned to at least partially include methoxy on Cu sites. Since very similar peaks were also seen for methoxy on a pure ZnO powder [8], we must conclude that these vibrational peaks are not very sensitive to the site of methoxy binding. This seems also clear based on comparison to very similar spectra on Cu single crystals [11,13] and Ni(111) [40].

The Cu-bound formate species reported in the infrared studies above on Cu/ZnO [7,8] was also reported after methanol exposure to oxygen-pretreated pure Cu powder by some of the same authors [8]. However, it is not seen here, even on thick Cu films, nor was it seen on oxygen-predosed Cu single crystals [10,11,16]. Sometimes it actually has been seen on Cu single crystals, but this has been attributed to formaldehyde impurity in the methanol [10,16]. This suggests that the presence of the Cu-bound formate species reported in the infrared studies above might also be related to formaldehyde impurities. Its presence there and absence here and in the studies on Cu single crystals may also be due to pressure/dosing differences, since the exposures used in the vibrational studies on high-area Cu/ZnO were much, much larger.

This comparison with results on high-area Cu/ZnO catalysts generally shows that these "real catalysts" have far more Zn^{2+} sites available for chemisorption than does the model catalyst we have prepared here, when compared on a per unit area basis. This is, of course, not unexpected given the ZnO plane used in this model catalyst.

5. Conclusions

On clean ZnO(000$\bar{1}$)-O and on clean Cu films on ZnO(000$\bar{1}$)-O, methanol is adsorbed molecularly at 125 K, desorbing with no measurable dissociation below 300 K. The desorption temperature is at ~ 200–260 K for atom-thin Cu 2D islands, resembling Cu(110), but at ~ 155 K on annealed, multilayer Cu islands, resembling Cu(111). On oxygen-predosed films thicker than one Cu atom, methanol reacts to form adsorbed methoxy species, which themselves decompose at about 400 K to give formaldehyde and hydrogen TPD peaks, as well as small amounts of methanol from the combination of H_a with methoxy. This is consistent with previous studies of methanol on single crystal Cu surfaces. No formate or CO_2 was found by TPD. Upon annealing to above 800 K, the methoxy decomposition peaks decrease dramatically in area, consistent with severe clustering of the Cu from flat islands to smaller, thicker islands which only cover a small fraction of the surface. There is some evidence that oxygen or methoxy chemisorption may redisperse these thick Cu islands, thus increasing their surface area. The methoxy decomposition temperature for Cu islands that have been annealed to ~ 600–750 K and are several atoms thick is 393 K, very similar to the value of 385 K seen on Cu(111). Oxygen-predosed Cu 2D islands that are only one Cu atom thick showed no clear evidence for a methoxy species in TPD. These results, together with our earlier study of water dissociation, show that oxygen atoms on atom-thin Cu islands are poorer Brønsted bases than oxygen adatoms on bulk Cu. No other special chemistry is seen due to Cu–ZnO interactions except for: (1) slight unexplained shifts in the peak temperature for methoxy decomposition on unannealed and severely annealed Cu films, and (2) spillover of hydrogen produced on the Cu islands into the near bulk of the ZnO.

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