Oxidation of methanol on the surfaces of model Cu/ZnO catalysts containing Cu^{1+} and Cu^0 species

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Interaction of CH_3OH with Cu clusters deposited on ZnO films grown on a Zn foil as well as on a ZnO(0001)–Zn crystal, has been examined by X-ray photoelectron spectroscopy. On clean Cu clusters, reversible molecular adsorption or formation of CH_3O is observed. However if the Cu clusters are pretreated with oxygen, both CH_3O and $HCOO^-$ species are produced. Model Cu/ZnO catalyst surfaces, containing both Cu^{1+} and Cu^0 species, show interesting oxidation properties. On a Cu^0-rich catalyst surface, only CH_3O species is formed on interaction with CH_3OH. On a Cu^{1+}-rich surface, however, $HCOO^-$ ion is the predominant species.

Keywords: methanol oxidation, Cu/ZnO catalysts, XPS, intermediate species, methanol–surface interaction

1. Introduction

Synthesis of methanol on Cu/ZnO catalysts is a problem of great contemporary interest in surface science and catalysis [1–5]. One of the important steps in the synthesis involves the hydrogenation of the formate ion, produced by the interaction of CO/CO_2 and H_2 with the catalyst surface. Formate ion along with formaldehyde and methoxy species are known to be produced by the oxidation of methanol on Cu surfaces containing oxygen and this surface reaction is also of considerable interest as evidenced from the recent literature [6–11]. Methanol gets dissociated even on clean Cu surfaces to give methoxy and hydrogen species which recombine to form methanol during desorption [12,13]. In the presence of oxygen, the methoxy radical formed on the Cu surface is further oxidized to H_2CO and then to HCOOH or $HCOO^-$ [6,10,11,14]. The formate ion is generally formed around 290 K or above. The presence of excess oxygen during the oxidation of CH_3OH on a Cu(110) surface seems to favour the formation of H_2CO, whereas the formation of $HCOO^-$ is favoured in methanol-rich mixtures [6,11]. Interaction of CH_3OH with Cu/ZnO films appears to lead to the formation of the formate ion [13], H_2CO and the methoxy species [15].

X-ray photoelectron spectroscopy (XPS) in the C(1s) region is ideally suited to study the oxidation of methanol on Cu and other metal surfaces since there are characteristic C(1s) binding energies for the different species. Thus, the C(1s) binding energies of adsorbed CH_3OH, CH_3O, and $HCOO^-$ are 286.8, 285.8 and 288 eV respectively [8,16]. We were interested in carrying out a XPS study of the oxidation of methanol on Cu/ZnO catalyst surfaces. For this purpose, we have prepared Cu/ZnO surfaces in situ in the sample preparation chamber of an electron spectrometer, by first growing a thick layer of ZnO on a clean Zn surface and depositing Cu clusters on ZnO/Zn by resistive evaporation, followed by the oxidation of the Cu clusters to Cu^{2+} and subsequent reduction in hydrogen to obtain surfaces comparable to those in real catalysts. By varying the size of the Cu clusters and the reduction conditions, it was possible to prepare surfaces with different proportions of Cu^{1+} and Cu^0 species. This is important since it is known that the Cu^{1+} species plays an important role in CH_3OH synthesis [1–4]. We have investigated the interaction of methanol with the model Cu/ZnO catalyst surfaces so prepared with different Cu^{1+}/Cu^0 ratios. For the purpose of comparison, we have also examined the interaction of CH_3OH with Cu clusters deposited on ZnO/Zn and ZnO(0001)–Zn surfaces, without subjecting them to oxidation and reduction. The present study is somewhat different from that of Fu and Somorjai [17], who studied the interaction of methanol on a model system produced by depositing ZnO islands on Cu(110) surfaces.

2. Experimental

The surface of a clean Zn foil was oxidized in the sample preparation chamber of a VG ESCA 3 MkII spectrometer by treatment with oxygen at 450 K to obtain a ZnO layer of 10 Å thick or greater. On such ZnO/Zn surfaces, different coverages of Cu were deposited. Cu clusters were also deposited at room temperature under UHV conditions, by the resistive

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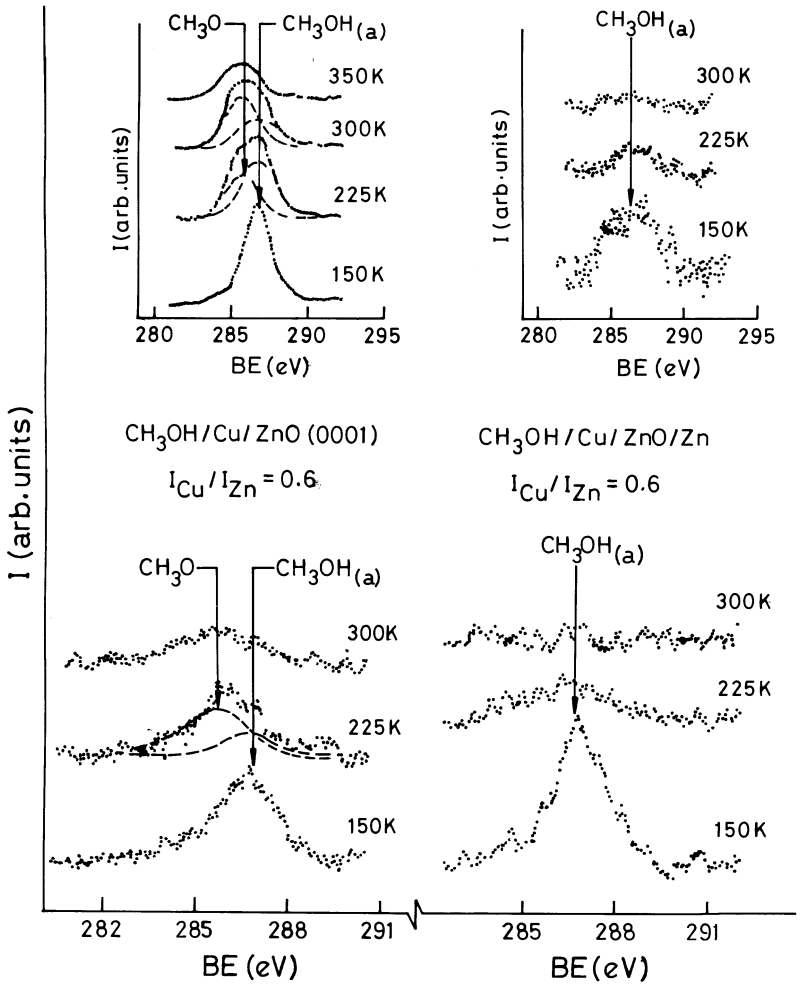

Figure 1. C(1s) spectra of CH_3OH adsorbed on Cu clusters ($I_{Cu}/I_{Zn} = 0.6$) deposited on (a) the surface of a ZnO(0001)–Zn crystal and (b) on ZnO/Zn. The insets show C(1s) spectra of CH_3OH adsorbed on the corresponding ZnO surfaces (without any Cu).

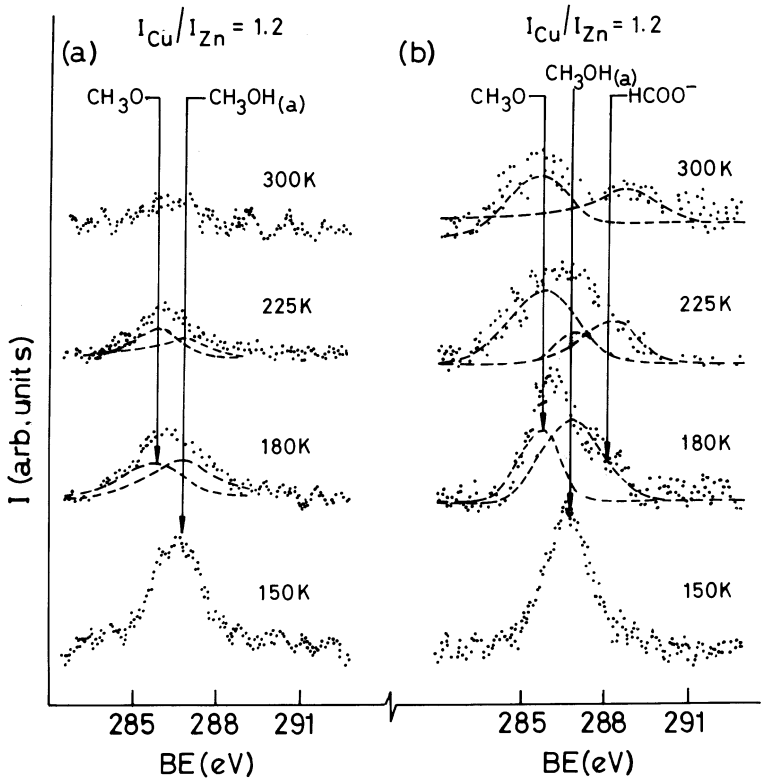

Figure 2. C(1s) spectra of CH_3OH adsorbed on (a) clean Cu clusters ($I_{Cu}/I_{Zn} = 1.2$) and (b) on oxygen predosed (200 L, at 300 K) Cu clusters ($I_{Cu}/I_{Zn} = 1.2$).The Cu clusters were deposited on ZnO/Zn surfaces.

evaporation of high-purity Cu metal wound on a thoroughly degassed tungsten filament on a Zn-terminated ZnO(0001) surface (ATRA MET inc.). It is known that diffusion of Cu through such a ZnO layer at room temperature does not occur when the thickness of the oxide layer is ~10 Å [18]. We have quantified the coverage of Cu by means of the ratio of the intensities of the Cu($2p_{3/2}$), and the Zn($2p_{3/2}$) features. Methanol (Merck, spectroscopic grade) was further purified on a UHV gas handling system using several freeze–pump–thaw cycles. Adsorption of methanol was carried out by exposing the surfaces to the vapour at 80 K for a coverage of 15 L (1 L = 10^{-6} Torr s). We have examined the interaction of methanol with Cu clusters deposited on ZnO/Zn as well as on a ZnO(0001)–Zn crystal, with I_{Cu}/I_{Zn} ratios of 0.6 and 1.2, corresponding to surface Cu concentrations of 2.91×10^{15} atoms cm^{-2} and 5.8×10^{15} atoms cm^{-2}, respectively [19].

In order to investigate the interaction of methanol with the model catalyst surfaces, we prepared different surfaces by depositing Cu clusters on ZnO/Zn corresponding to I_{Cu}/I_{Zn} ratios of 2.5, 1.5 and 0.9 (equivalent to surface Cu concentrations of 1.2×10^{16}, 7.6×10^{15} and 4×10^{15} atoms cm^{-2}, respectively). The Cu clusters so deposited were oxidized by treatment with oxygen at 400 K. The resulting surface contained mainly Cu^{2+} species as revealed by the Cu (LMM) Auger spectra and Cu($2p_{3/2}$) core-level spectra. This surface was reduced by treatment with hydrogen at 450 K. The Cu (LMM) Auger spectra of such surfaces showed that they contain Cu^0, Cu^{1+} as well as Cu^{2+}

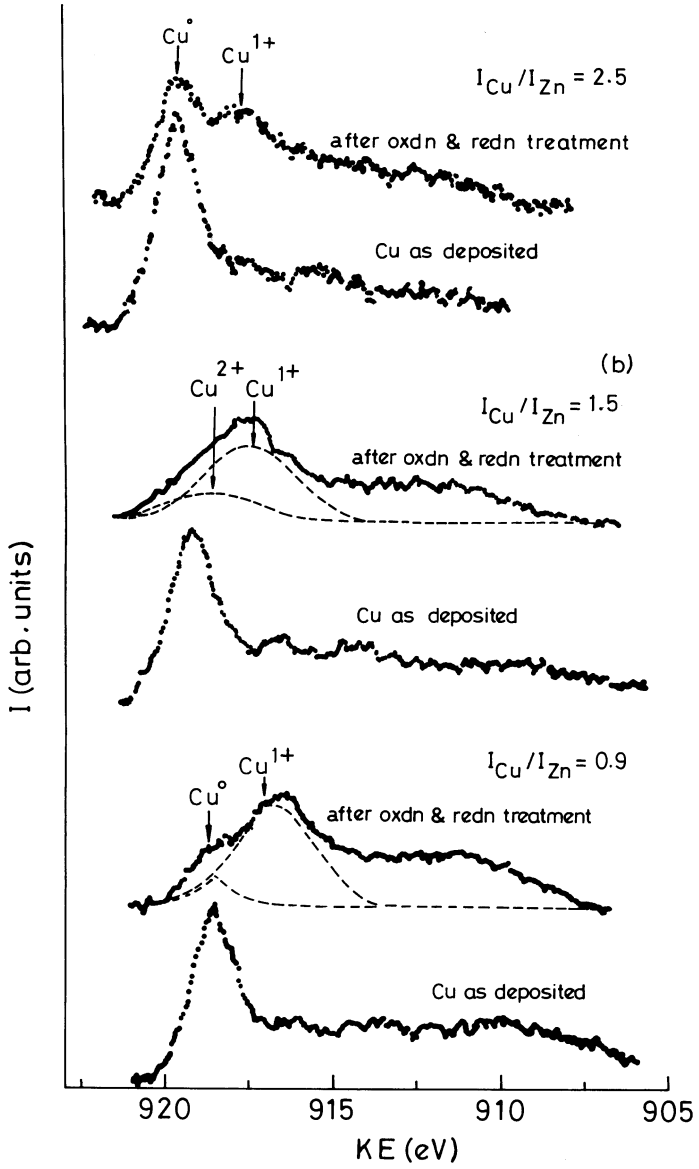

Figure 3. Cu (LMM) Auger spectra of Cu clusters deposited on ZnO/Zn and subjected to in situ oxidation followed by hydrogen reduction: (a) $I_{Cu}/I_{Zn} = 2.5$, (b) $I_{Cu}/I_{Zn} = 1.5$ and (c) $I_{Cu}/I_{Zn} = 0.9$. The Auger features due to Cu^0, Cu^{1+} and Cu^{2+} are indicated.

(the characteristic kinetic energies being 918.7, 916.6 and 917.7 eV respectively [20]), the relative proportion varying with the initial coverage of Cu and the extent of reduction. We could prepare surfaces containing different proportions of the three Cu species. The Cu^{1+}/Cu^0 ratio was higher on the surface when the Cu coverage was small ($I_{Cu}/I_{Zn} = 0.9$) compared to that on the surface with a I_{Cu}/I_{Zn} of 2.5. Hydrogen reduction at 400 K enabled us to obtain a surface containing a small proportion of Cu^{2+} along with Cu^{1+} and Cu^0. Interaction of methanol (15 L) was investigated with three different Cu/ZnO surfaces.

3. Results and discussion

In figure 1a, we show the C(1s) core-level spectra of CH_3OH adsorbed on Cu clusters ($I_{Cu}/I_{Zn} = 0.6$) deposited on a ZnO(0001)–Zn crystal. At 80 K, CH_3OH is physisorbed on the surface giving a C(1s) feature at 287.2 eV. On warming to 150 K, the C(1s) feature characteristic of chemisorbed CH_3OH at 286.8 eV appears (figure 1a). At 225 K, a feature due to the CH_3O species manifests itself at 285.8 eV. This feature gains in intensity when warmed to 300 K. This behaviour is to be contrasted with that of Cu clusters deposited ($I_{Cu}/I_{Zn} = 0.6$) on the ZnO layer grown on a polycrystalline Zn foil (ZnO/Zn). Here also, methanol is molecularly adsorbed at 150 K with a C(1s) binding energy of 286.8 eV, but on warming the surface to 300 K, methanol desorbs molecularly from the surface without the formation of the methoxy species (figure 1b). This behaviour of CH_3OH is similar to that found on clean Cu surfaces [12,13]. It is instructive to examine the adsorption of CH_3OH on pure ZnO surfaces (without any Cu). On the surface of the ZnO(0001)–Zn crystal, the CH_3O species is formed around 225 K (see inset of figure 1a), while on the ZnO/Zn surface, methanol is molecularly adsorbed at 150 K, but desorbs well below room temperature (see inset of figure 1b). Such a difference in the interaction of CH_3OH on Zn-terminated and O-terminated ZnO surfaces has been noted in the literature [21–23].

When the Cu clusters deposited on ZnO/Zn are large ($I_{Cu}/I_{Zn} = 1.2$), the initial chemisorption of methanol at 150 K is followed by the formation of CH_3O species at higher temperatures (figure 2a) and total desorption above 300 K. In figure 2b, we show the interaction of methanol with Cu/ZnO/Zn predosed with O_2 (200 L at 300 K). Here we see the chemisorbed molecular species

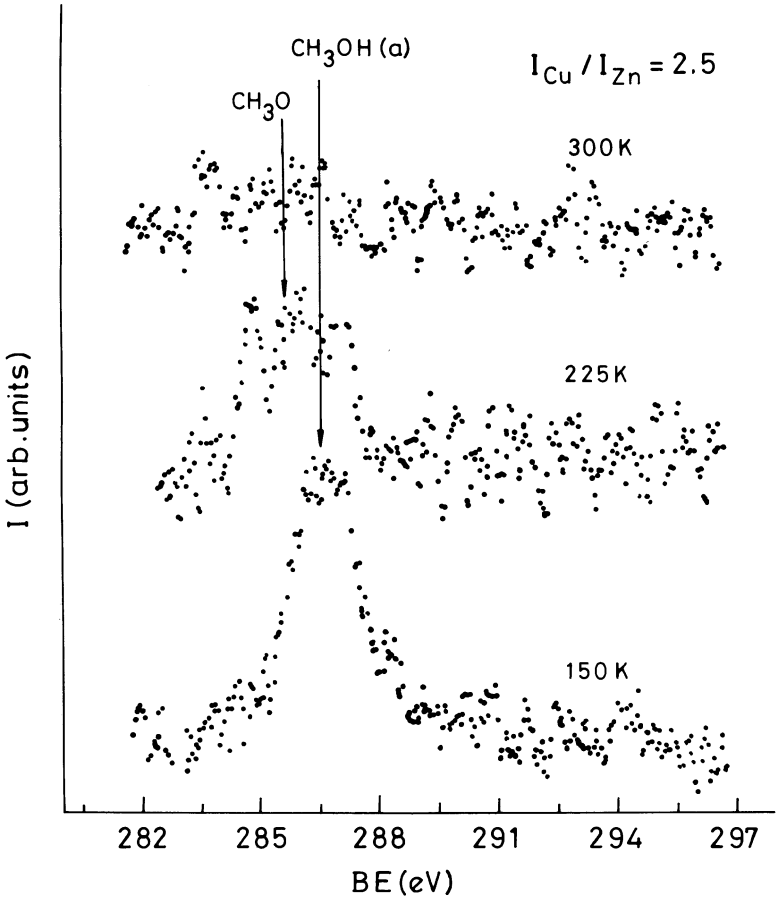

Figure 4. C(1s) spectra of CH_3OH adsorbed on a Cu/ZnO/Zn model catalyst surface with $I_{Cu}/I_{Zn} = 2.5$ (Cu^0-rich surface).

at 150 K, followed by the CH_3O species at 180 K and the subsequent formation of the formate species at 225 K, with a C(1s) feature at 288 eV. These results are consistent with methanol interaction studies of oxygen-treated single-crystal Cu surfaces reported in the literature [6,10,11,14].

The most interesting part of the present study relates to the interaction of CH_3OH with the model catalyst surfaces, prepared by the oxidation of Cu clusters in an oxygen atmosphere at 400 K, followed by hydrogen reduction at 450 K. In figure 3 we show three typical catalyst surfaces prepared in this manner with different proportions of Cu^{1+}, Cu^0 and Cu^{2+} species. In figure 3a where the initial Cu coverage corresponds to I_{Cu}/I_{Zn} of 2.5, the Cu (LMM) Auger spectrum shows the surface to be rich in Cu^0 compared to Cu^{1+}. However, the Auger spectrum of the surface depicted in figure 3b ($I_{Cu}/I_{Zn} = 1.5$) shows the presence of some Cu^{2+} in addition to Cu^{1+} and a very small proportion of Cu^0. In figure 3c, where $I_{Cu}/I_{Zn} = 0.9$, we have a surface rich in Cu^{1+}. Interaction of methanol with the Cu^0-rich surface (figure 3a) shows molecular adsorption at 150 K, followed by the formation of CH_3O at 225 K and total desorption from the surface below 300 K (figure 4). This behaviour is similar to that found with Cu clusters deposited on ZnO/Zn (figures 1b and 2a). Interaction of CH_3OH with a surface containing some Cu^{2+} in addition to Cu^{1+} (figure 3b) results in the chemisorption of CH_3OH at 150 K, the formation of CH_3O at 180 K and further oxidiation to formate ion at 225 K (figure 5). The proportion of the formate species increases at 300 K. This situation is close to that found on oxygen-dosed Cu clusters (figure 2b). Interaction of CH_3OH with the Cu^{1+}-rich surface (figure 3c) gives rise to the formation of formate ion around 225 K, with all the CH_3O species getting transformed to $HCOO^-$ around 300 K (figure 6). This surface shows the highest proportion of $HCOO^-$, of all the surfaces studied by us, indicating the crucial role of Cu^{1+}. It may be noted that on such Cu^{1+}-rich model catalyst surfaces, CO readily transforms to CO_2^- [24].

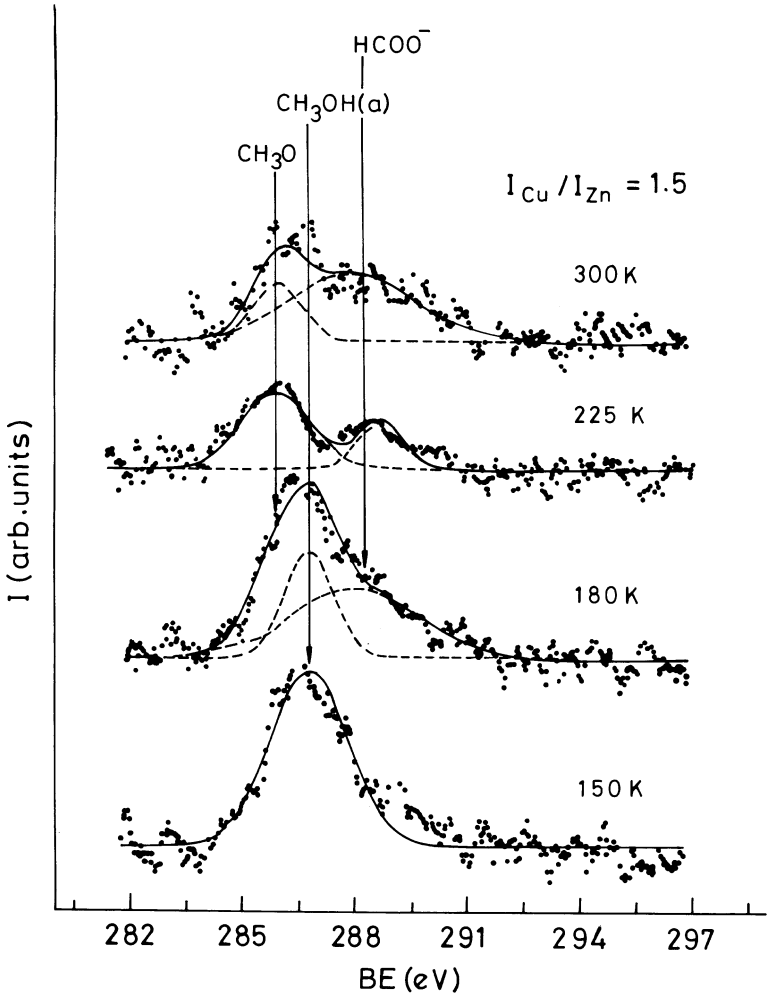

Figure 5. C(1s) spectra of CH_3OH adsorbed on a Cu/ZnO/Zn model catalyst surface with $I_{Cu}/I_{Zn} = 1.5$.

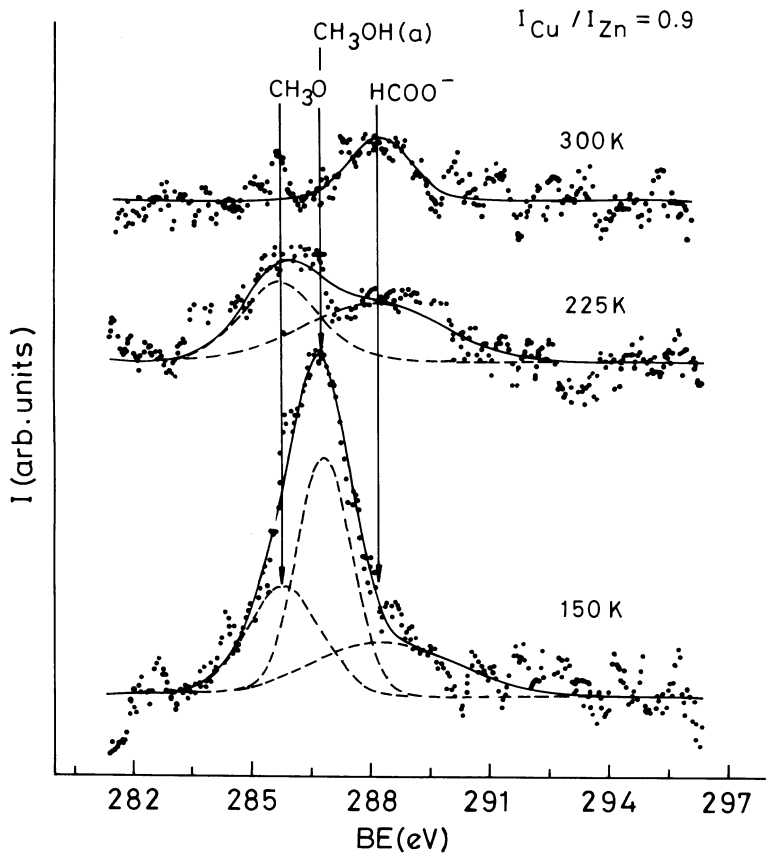

Figure 6. C(1s) spectra of CH_3OH adsorbed on a Cu/ZnO/Zn model catalyst surface with $I_{Cu}/I_{Zn} = 0.9$ (Cu^{1+}-rich surface).

4. Conclusions

(i) CH_3OH exhibits reversible molecular adsorption on clean Cu clusters deposited on ZnO surfaces. When the Cu cluster size is relatively large, CH_3O species, stable up to 300 K, is formed. If the Cu clusters are pretreated with oxygen, formate ion is formed along with CH_3O.

(ii) CH_3OH does not interact strongly with oxygen-terminated ZnO, but gives rise to CH_3O species on zinc-terminated ZnO surfaces.

(iii) Cu/ZnO catalysts prepared in situ in the preparation chamber of the electron spectrometer, by depositing Cu clusters on a thick ZnO layer grown on a Zn foil, followed by oxidation and hydrogen reduction, provide good model surfaces, containing both Cu^{1+} and Cu^0 species. The proportion of Cu^{1+} and Cu^0 can be varied depending on the reduction conditions as well as the initial Cu coverage.

(iv) CH_3OH is oxidized to CH_3O on a Cu^0-rich surface of the model catalyst, while on a Cu^{1+}-rich surface the initially formed CH_3O species is further oxidized to formate ion. This observation suggests that there is a link between the Cu^{1+}/Cu^0 ratio on the catalyst surface and the formation of CH_3O and $HCOO^-$ species.

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