

## Facile C–O Bond Scission in Alcohols on Zn Surfaces

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Interaction of methanol, ethanol, and 2-propanol with polycrystalline as well as (0001) surfaces of Zn has been investigated by photoelectron spectroscopy and vibrational energy loss spectroscopy. All the alcohols show evidence for the condensed species along with the chemisorbed species at 80 K. With increase in temperature to ~120 K, the condensed species desorbs, leaving the chemisorbed species which decomposes to give the alkoxy species. The alkoxy species is produced increasingly at lower temperatures as we go from methanol to 2-propanol, the 2-propoxy species occurring even at 80 K. The alkoxy species undergo C–O bond scission giving rise to a hydrocarbon species and oxygen. The C–O bond cleavage occurs at a relatively low temperature of ~150 K. The effect of preadsorbed oxygen is to stabilize the methoxy species and prevent C–O bond scission. On the other hand, coadsorption of oxygen with methanol favors the formation of the methoxy species and gives rise to hydrocarbon species arising from the C–O bond scission even at 80 K.

### Introduction

Interaction of methanol with transition metal surfaces has been investigated by several workers because of its relevance to environmental pollution and industrial processess. Rufael et al.<sup>1</sup> have reported that the thermal decomposition of methanol on an Fe(110) surface occurs at 100 K, giving rise to the methoxy species and hydrogen. The methoxy species undergoes dehydrogenation giving H<sub>2</sub> and CO around 400 K. Levis et al.<sup>2</sup> found that methanol decomposes on a Pd(111) surface to yield CH<sub>3</sub>(a), OCH<sub>3</sub>(a), and H<sub>2</sub>O(a) around 125 K, the CH<sub>3</sub>(a) species showing high stability on the surface. Kruse et al.<sup>3</sup> observed that methanol forms mainly the methoxy species, followed by its decomposition to CO and H<sub>2</sub> on the Pd(111) surface, with negligible C–O bond scission. Rebholz et al.,<sup>4</sup> however, found evidence for C–O bond scission on the Pd(111) surface, giving the CH<sub>3</sub>(a) species. On a Pt(110) surface, Wang and Masel<sup>5</sup> have reported C–O bond scission around 140 K, giving rise to (CH)<sub>x</sub> type adsorbed species which finally gave CH<sub>4</sub>, H(a), and C(a), in addition to higher hydrocarbons at temperatures well above 200 K. On Co overlayers deposited on Mo(110), methoxy is the major species at 250 K, giving CO at 350 K, followed by dissociation of CO to atomic carbon and oxygen.<sup>6</sup> Thermal decomposition of methanol on the (100) surface of NiAl, which predominantly consists of Al sites, gives stable methoxy species around 120 K.<sup>7</sup> In contrast, on the NiAl(110) surface, H<sub>2</sub>, CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> are formed at high temperatures. On a NiAl-(111) surface, CH<sub>3</sub>OH transforms to the methoxy species which then decomposes to H<sub>2</sub>, CO, CH<sub>4</sub>, etc.<sup>8</sup> CO and CH<sub>4</sub> appear to result from the decomposition of CH<sub>3</sub>OH on the Al site. On FeAl(110) also, the CH<sub>3</sub>O species formed at 110 K, decomposes to H<sub>2</sub> and CH<sub>4</sub> above 400 K.<sup>9</sup> It has been suggested that the nature of the transition metal underlayer in the transition metal–Al systems affects the C–O bond energy.<sup>10</sup> On the Al(100) surface itself, the C–O bond of methanol is expected to be rather weak decomposing to the CH<sub>3</sub>.<sup>11</sup>

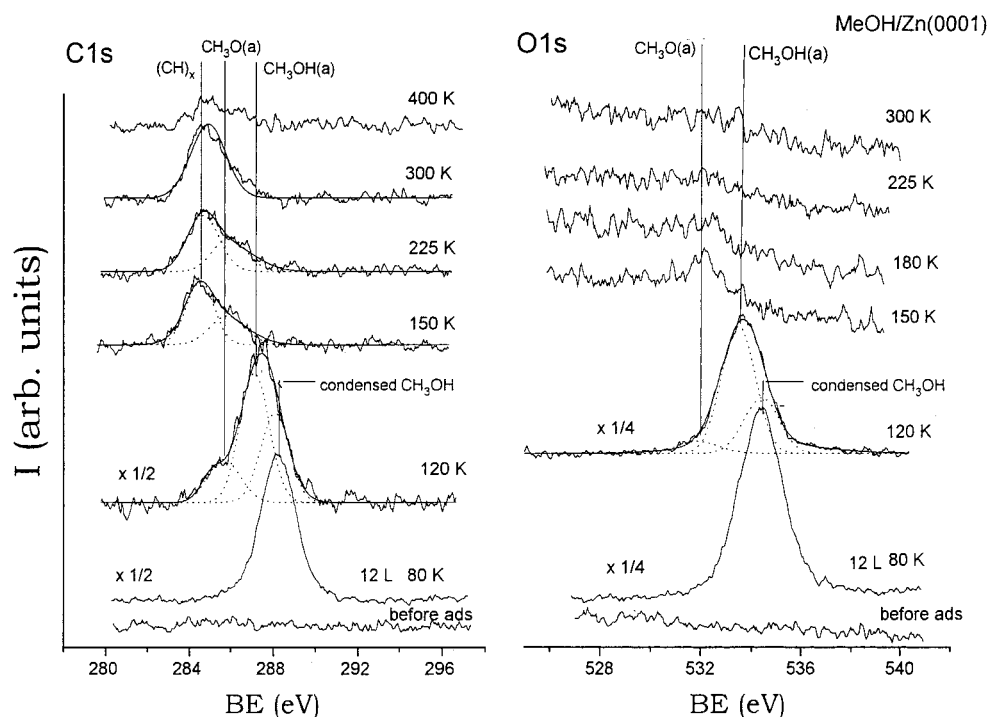
Benziger and Madix<sup>12</sup> reported that interaction of ethanol with a Fe(100) surface yields the alkoxy species, just like methanol, at or below room temperature which decomposes to CO and H<sub>2</sub> or undergoes C–C or C–O bond scission. Bowker and Madix<sup>13</sup> reported that on a Cu(110) surface, the stable ethoxy species formed by ethanol further reacts to yield the corresponding aldehyde. On a Rh(111) surface, Houtman and Barteau<sup>14</sup> found that decomposition of ethanol does not proceed by dehydrogenation but instead C–C bond scission occurs in the ethoxy species. On a Pd(111) surface, Davis and Barteau<sup>15</sup> observed that while methanol gives rise to CO and H<sub>2</sub>, ethanol underwent C–C bond scission to form CO, H<sub>2</sub>, and hydrocarbons. On a Ni(111) surface, ethanol forms only the ethoxy species.<sup>16</sup> On a Pt(111) surface, Sexton et al.<sup>17</sup> report that C<sub>1</sub>–C<sub>4</sub> alcohols undergo complete dissociation to CO, H<sub>2</sub>, and C or undergo C–C bond scission. Evidence for C–C bond scission to form methane and other related species has also been reported on the Pt(331) surface.<sup>18</sup> While the alkoxy species is not formed on interaction of 2-propanol with an Fe(110) surface, the 2-propoxy species is formed on a Cu(110) surface.<sup>12,13</sup> On a Pd(110) surface, however, 2-propanol undergoes selective dehydrogenation to form acetone in addition to giving CH<sub>4</sub>, CO and H<sub>2</sub>.<sup>15</sup> Wiegand et al.<sup>19</sup> studied the interaction of 1-propanol and 2-propanol on Mo(110) surfaces and found the formation of propoxy species in both the cases. This species is stable up to quite high temperatures, transforming to propene due to C–O (as well as C–H) bond scission.

We have investigated the interaction of CH<sub>3</sub>OH with surfaces of Zn(0001) as well as polycrystalline Zn by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and vibrational electron energy loss spectroscopy (VEELS) and examined the effects of predosed oxygen as well as coadsorbed oxygen on the decomposition. Furthermore, we have studied the decomposition of ethanol and 2-propanol on Zn surfaces by these techniques. The primary purpose of this study is to examine whether C–O bond scission is the major transformation occurring during the decomposition of alcohols on Zn surfaces. It was considered possible that the low sticking coefficient for oxygen on zinc surfaces<sup>20</sup> may influence the C–O

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**Figure 1.** C(1s) and O(1s) spectra of CH<sub>3</sub>OH adsorbed on Zn(0001) surface. CH<sub>3</sub>OH was first adsorbed at 80 K and the surface progressively warmed to 400 K.

bond scission or the escape of oxygen resulting from the scission. In the case of CH<sub>3</sub>OH, abstraction of H and C–O bond scission would be expected to yield CH<sub>3</sub>O and CH<sub>3</sub> species, respectively. In the case of ethanol, however, we have to consider the possibility of C–O as well as C–C bond scission, the products depending on the mode of decomposition. The same would be true of 2-propanol. The present study, however, demonstrates that the C–O bond scission, following hydrogen abstraction, is the only mode of decomposition of alcohols on Zn surfaces, the alkoxy species initially produced giving rise to hydrocarbon species, at rather low temperatures. The alkoxy species is most stable in the case of 2-propanol and coadsorption of oxygen favors the C–O bond scission.

### Experimental Section

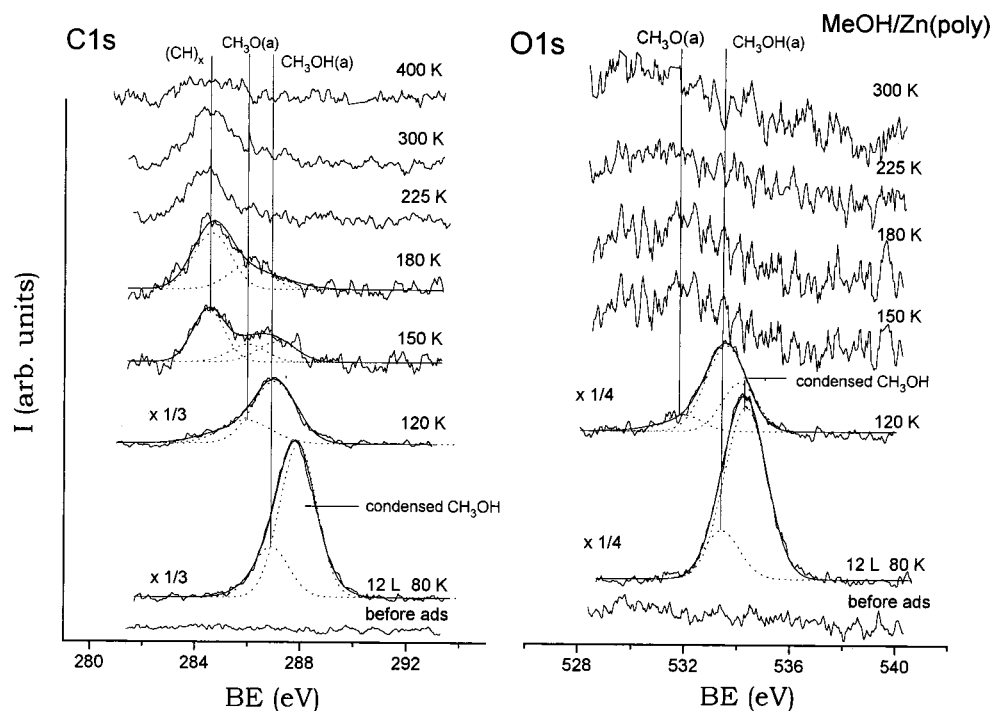
Photoelectron spectroscopic measurements were carried out with a VG ESCA 3 MkII spectrometer fitted with a sample preparation chamber at a base pressure of  $\sim 2 \times 10^{-10}$  Torr. Al K $\alpha$  (1486.6 eV) and He II (40.8 eV) radiation were employed for XPS and UPS measurements, respectively. VEELS measurements were carried out with a VSW spectrometer attached with a EM45 electron monochromator in specular mode with an electron beam energy of 5 eV at a base pressure of  $2 \times 10^{-10}$  Torr. A typical energy resolution of 150 cm<sup>-1</sup> was achieved during the data collection. Adsorption studies were carried out on a high-purity ( $\sim 99.99\%$ ) polycrystalline zinc foil from Johnson-Matthey as well as on the (0001) face of a single crystal of zinc (purity of 99.999%) obtained from Atomergic Chemicals Corp. Both the surfaces were cleaned in situ in the preparation chamber of the instrument by Ar<sup>+</sup> ion etching followed by annealing at 450 K until clean surfaces, devoid of carbon and oxygen, were obtained. Low Ar ion power (500–1000 eV) was used for etching the single-crystal surface in order to avoid sample damage.

All the alcohols studied here are of spectroscopic grade and were further purified on a UHV gas handling system using

several freeze–pump–thaw cycles. Adsorption of methanol, ethanol, and 2-propanol was carried out by exposing the surfaces to the vapor at 80 K for a coverage of 12 langmuir (1 langmuir =  $10^{-6}$  Torr s). The oxygen-covered Zn surface was prepared by exposing the clean zinc surface to 50 langmuir O<sub>2</sub> at 80 K. For coadsorption studies, a 3:1 CH<sub>3</sub>OH–O<sub>2</sub> mixture was exposed to the atomically clean polycrystalline zinc surface at 80 K for a coverage of 100 langmuir.

### Results and Discussion

**Methanol.** In Figure 1, we show the C(1s) and O(1s) spectra of methanol adsorbed on the Zn(0001) surface at 80 K and the effect of subsequent warming of the surface up to 400 K. At 80 K, there is an intense, broad feature centered at 288 eV in the C(1s) spectrum, essentially due to the condensed species, with a small proportion of the chemisorbed species at a slightly lower binding energy (287 eV). The literature values<sup>1,21,22</sup> of the C(1s) binding energies for condensed and chemisorbed CH<sub>3</sub>OH are 287.7 and 286.8 eV, respectively. When the surface is warmed to 120 K, there is a shift of the main feature to 287 eV, suggesting the presence of a considerable proportion of the chemisorbed species. In addition, there is a weak C(1s) feature centered around 286 eV which we assign to the methoxy species. The literature value<sup>1,21,22</sup> of the C(1s) binding energy for the methoxy species is 285.8 eV. The O(1s) spectrum shows an intense feature at 534.3 eV due to the condensed species at 80 K and a feature at 533.5 eV due to the chemisorbed species (the literature value<sup>1</sup> being 533.6 eV) at 120 K. We also see a weak feature around 532 eV due to OCH<sub>3</sub>(a) at 120 K. At 150 K, only the 532 eV feature remains in the O(1s) spectrum. Thus, a major proportion of the chemisorbed species desorbs molecularly at 150 K leaving behind a small amount of methoxy species on the surface. In the C(1s) spectrum, besides the methoxy species we see a species with a feature at a still lower binding energy (285 eV). On warming the surface to 180 K, the feature due to the methoxy species decreases in intensity in both the

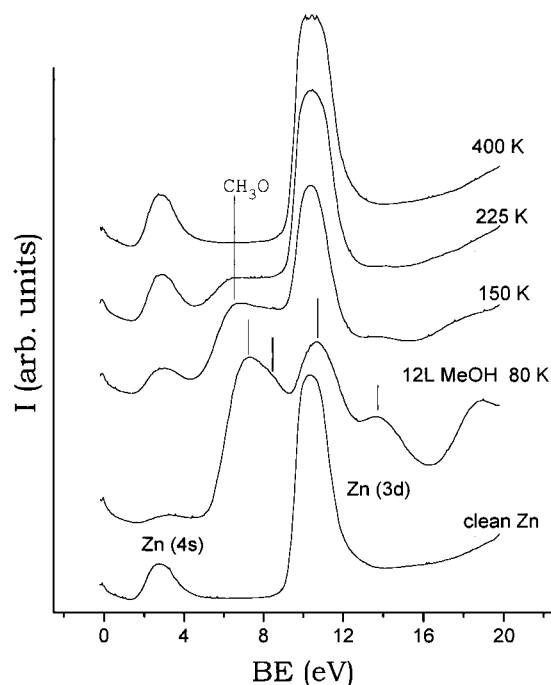


**Figure 2.** C(1s) and O(1s) spectra of  $\text{CH}_3\text{OH}$  adsorbed on a polycrystalline Zn surface.  $\text{CH}_3\text{OH}$  was first adsorbed at 80 K and the surface progressively warmed to 400 K.

C(1s) and the O(1s) spectra and becomes even smaller at 225 K. On the other hand, the 285 eV feature remains up to 400 K. The increase in intensity of the 285 eV feature correlates with the decrease in the intensity of the methoxy species up to 300 K. We assign the 285 eV feature due to  $\text{CH}_3$  or  $(\text{CH})_x$  type of species. We do not see any visible O(1s) feature resulting from the C–O bond scission above 225 K, possibly due to the subsurface diffusion of oxygen.<sup>23</sup>

We have studied the interaction of methanol with the surface of a polycrystalline Zn foil as well and show the C(1s) and O(1s) spectra in Figure 2. At 80 K, the condensed species with C(1s) and O(1s) features around 288 and 534.3 eV, respectively, are seen. At 120 K, these features become considerably weaker than on the single-crystal surface, and the features at 287 and 533.5 eV due to the chemisorbed species appear in the spectra. We also notice the emergence of the C(1s) feature at 286 eV and the O(1s) feature at 532 eV, due to the methoxy species at 120 K. With increase in temperature above 150 K, the features due to the methoxy species decrease in intensity, accompanied by the progressive emergence of the 285 eV feature due to the  $(\text{CH})_x$  species. The O(1s) spectra in Figures 1 and 2 suggest that the C–O bond scission occurs from 150 K onward, but the oxygen species produced is not clearly seen in the spectra. It is known from the literature<sup>20</sup> that the sticking coefficient of  $\text{O}_2$  on Zn surfaces is very low, but this may not be the reason. It is more likely that oxygen is present as a subsurface species.<sup>23</sup>

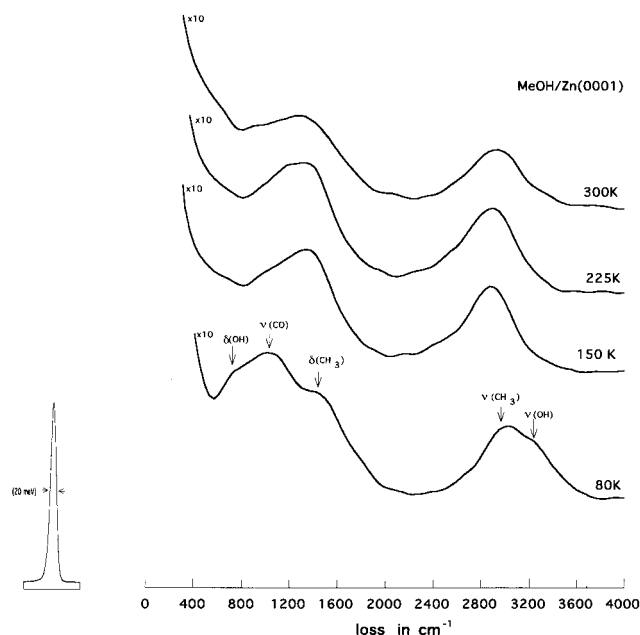
He II UPS studies of  $\text{CH}_3\text{OH}$  adsorbed on the polycrystalline Zn surface show changes which are consistent with the XPS results. In the UPS spectrum at 80 K, characteristic peaks of adsorbed  $\text{CH}_3\text{OH}$  are seen at 6.5, 8, 11, and 13.5 eV, respectively (see the features marked in Figure 3). On warming the surface to 150 K, only the feature at 6 eV due to the methoxy species remains. It is reported in the literature<sup>24,25</sup> that formation of the methoxy species is characterized by UPS peaks at 6 and 9.5 eV. We do not see the signal at 9.5 eV since it is masked by the intense Zn(3d) band around 10 eV. This feature due to



**Figure 3.** He II up-spectra of  $\text{CH}_3\text{OH}$  adsorbed on a polycrystalline Zn surface.  $\text{CH}_3\text{OH}$  was first adsorbed at 80 K and the surface progressively warmed to 400 K.

methoxy disappears above 225 K and no distinct feature due to the  $(\text{CH})_x$  species is seen because of the overlap with the Zn-(3d) band.

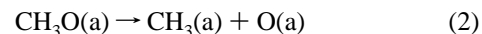
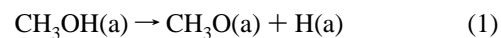
Results from photoelectron spectroscopic studies discussed above show that methanol transforms to the methoxy species on Zn surfaces, followed by the decomposition of the  $\text{OCH}_3$  species to hydrocarbon species. There is no evidence for the formation of CO. In order to confirm the results from XPS and UPS, we have studied the interaction of methanol with the Zn-(0001) surface by using vibrational electron energy loss



**Figure 4.** VEEL spectra of  $\text{CH}_3\text{OH}$  adsorbed on  $\text{Zn}(0001)$  surface at 80 K and progressively warmed to higher temperatures.

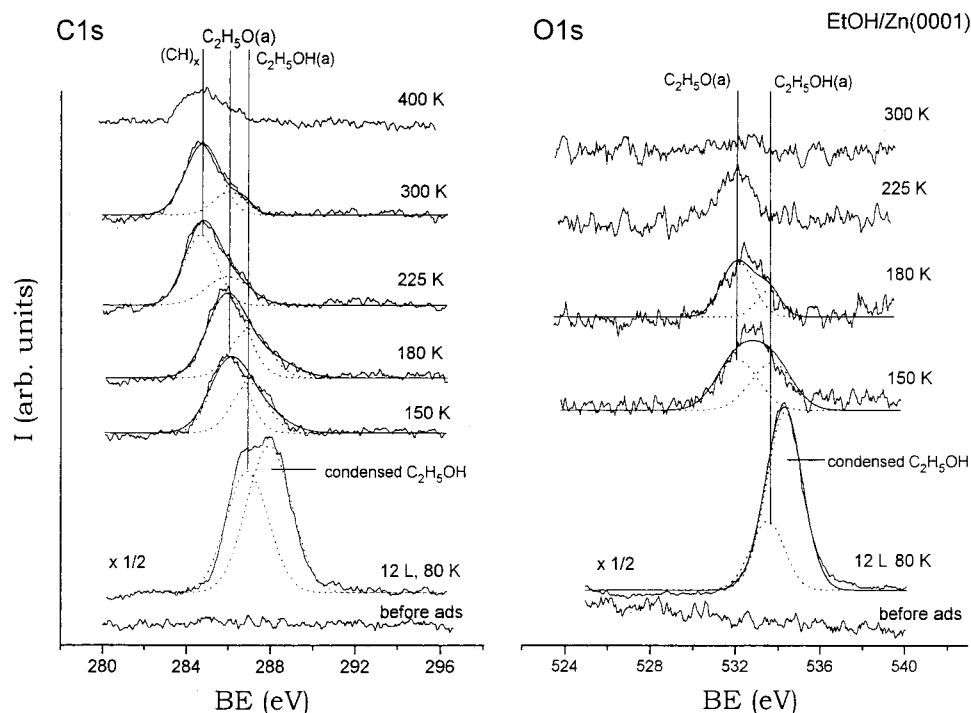
spectroscopy (VEELS). Adsorption of methanol on the clean  $\text{Zn}(0001)$  surface at 80 K gives a band due to OH stretching around  $3300\text{ cm}^{-1}$ , and another due to C–O stretching around  $1050\text{ cm}^{-1}$ , in addition to the bands due to the stretching and bending modes of the  $\text{CH}_3$  group at  $2900$  and  $1450\text{ cm}^{-1}$  respectively (see Figure 4). The  $3300\text{ cm}^{-1}$  band due to  $\nu(\text{OH})$  suggests extensive hydrogen bonding in the condensed phase. A band around  $750\text{ cm}^{-1}$  is seen due to the libration mode of OH group ( $\delta(\text{OH})$ ) at 80 K. On warming the surface to 150 K, the  $\nu(\text{OH})$  and  $\delta(\text{OH})$  bands disappear, suggesting that H abstraction occurs well below this temperature. We, however, see the bands due to  $\text{CH}_3$  and C–O groups. These changes are consistent with the presence of the methoxy species at 150 K

and the results agree with those of Sen and Rao.<sup>25</sup> At 225 K and above, only the bands due to the bending and stretching modes of the  $\text{CH}_3$  or  $(\text{CH})_x$  remain. The VEEL spectra show no evidence for carbon monoxide. Based on these studies we summarize the mechanism of decomposition of methanol on Zn surfaces to be as follows:



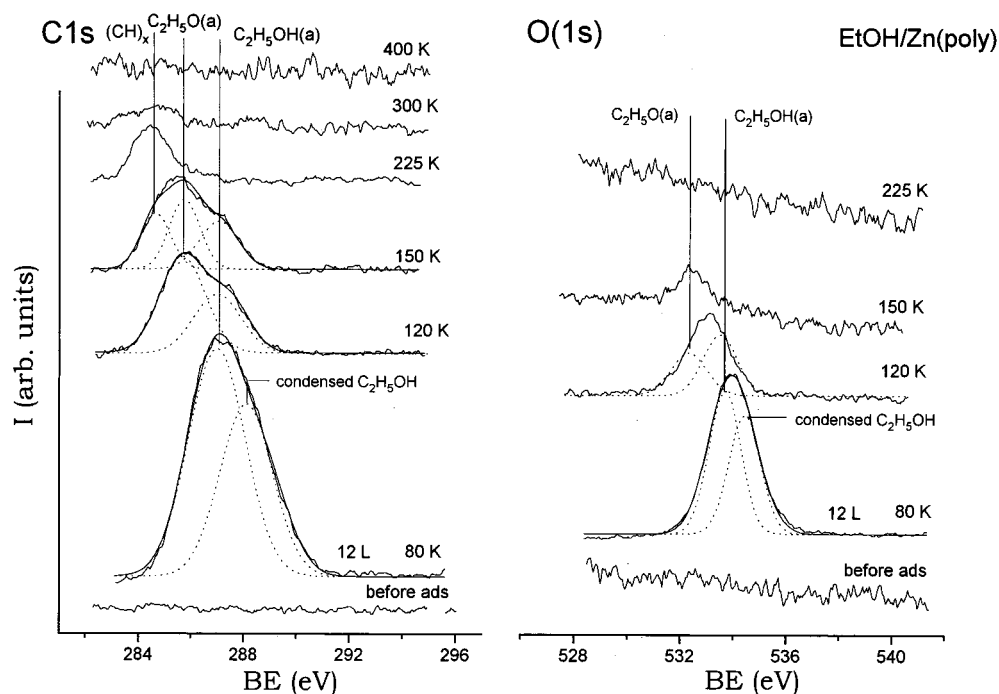
In order to examine whether the  $(\text{CH})_x$  type species are formed instantaneously on the Zn surface, we exposed 12 langmuirs of methanol at 150 K (the temperature at which we observe the appearance of the feature due to  $(\text{CH})_x$  in XPS). There was no adsorption on the surface under these conditions. At higher exposures (50 langmuirs), weak features around 287 and 533.4 eV characteristic of molecularly adsorbed methanol appeared in the  $\text{C}(1\text{s})$  and  $\text{O}(1\text{s})$  spectra. This observation indicates that adsorption at low temperatures is a prerequisite for C–O bond scission at higher temperatures. A noteworthy feature in the present study is the formation of the hydrocarbon species by C–O bond scission at a low temperature of 150 K. Such hydrocarbon species occur at much higher temperatures on other metal surfaces.

**Ethanol.** In Figure 5 we show the  $\text{C}(1\text{s})$  and  $\text{O}(1\text{s})$  spectra of ethanol adsorbed on  $\text{Zn}(0001)$  at 80 K, followed by progressive warming up to 400 K. The  $\text{C}(1\text{s})$  spectrum of ethanol at 80 K shows an asymmetric band which could be decomposed into two peaks centered around 288 and 287 eV due to the condensed and the chemisorbed species, respectively. On warming to 120 K, the condensed species desorbs almost completely. The intensity of the feature due to the chemisorbed species also decreases, accompanied by a new intense feature at 286 eV due to the ethoxy species. It is noteworthy that the concentration of the ethoxy species derived from the  $\text{C}(1\text{s})$  spectrum is considerable, compared to that of the methoxy



**Figure 5.**  $\text{C}(1\text{s})$  and  $\text{O}(1\text{s})$  spectra of  $\text{C}_2\text{H}_5\text{OH}$  adsorbed on  $\text{Zn}(0001)$  surface.  $\text{C}_2\text{H}_5\text{OH}$  was first adsorbed at 80 K and the surface progressively warmed to 400 K.

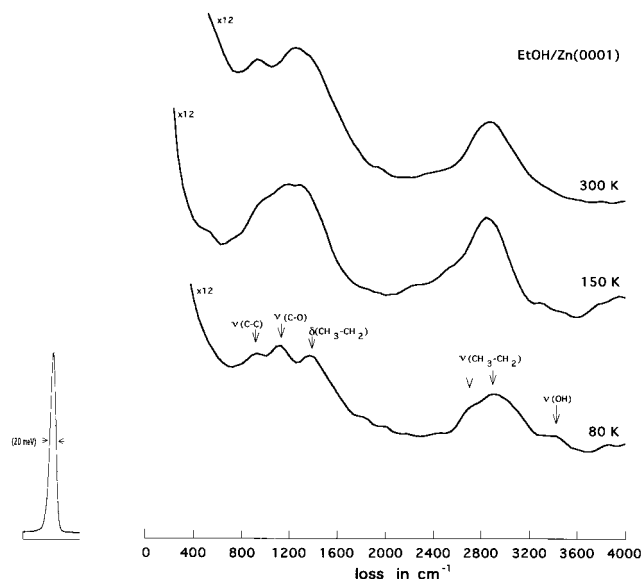




**Figure 6.** C(1s) and O(1s) spectra of  $\text{C}_2\text{H}_5\text{OH}$  adsorbed on a polycrystalline Zn surface.  $\text{C}_2\text{H}_5\text{OH}$  was first adsorbed at 80 K and the surface progressively warmed to 400 K.

species in Figure 1. On warming the surface to 225 K, the signal due to ethoxy decreases with the appearance of a feature at 285 eV due to  $\text{C}_2\text{H}_5$  or  $(\text{CH})_x$  type species. This feature remains even at 400 K, though weak in intensity, suggesting that part of the hydrocarbon may desorb from the surface at or below this temperature. The O(1s) spectrum at 80 K, shows a feature at 534 eV due to condensed ethanol along with a weak feature around 533.5 eV due to the chemisorbed species. On warming to 150 K, the 534 eV feature disappears completely while the peak due to chemisorbed ethanol remains, accompanied by the emergence of a 532 eV feature due to the ethoxy species. The O(1s) and C(1s) spectra at 225 K shows that some proportion of the adsorbed ethanol gets decomposed to ethoxy species and the remaining desorbs molecularly around 150 K. The core-level binding energy values of the different species are close to those quoted in the literature.<sup>12,13</sup> On warming to 300 K, we see no feature in the O(1s) spectrum due to an oxygen species, possibly due to the subsurface diffusion of oxygen as explained before.<sup>23</sup> These data are consistent with the C(1s) spectral features and suggest that on a Zn(0001) surface, ethanol gives rise to the ethoxy species, followed by the formation of  $\text{C}_2\text{H}_5$  or  $(\text{CH})_x$  type species around 225 K. There is no evidence for the formation of CO or a carbonyl compound.

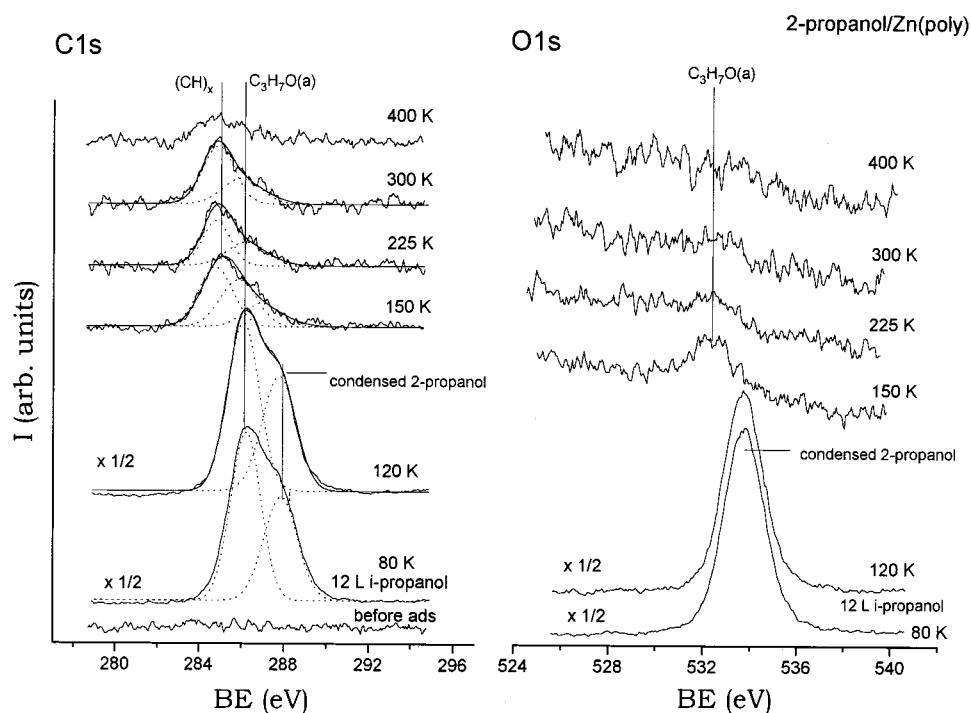
The results from the single-crystal surface are also corroborated by our observations on polycrystalline Zn (Figure 6). The major difference with the polycrystalline surface is that at 80 K there is a significant proportion of chemisorbed ethanol (287 eV in the C(1s) spectrum). On warming to 120 K, the feature at 286 eV due to the ethoxy species appears. We see a weak, but distinct, feature due to the  $(\text{CH})_x$  species at 150 K, unlike on the Zn(0001) surface. The ethoxy species is absent on the polycrystalline Zn surface at 225 K, giving only  $(\text{CH})_x$ -like species at this temperature and above. Around 400 K, the C(1s) signal is absent, suggesting that the hydrocarbon species desorbs at or below this temperature. The O(1s) spectra of ethanol adsorbed on polycrystalline Zn at 80 K shows features at 534 and 533.5 eV due to the condensed and the chemisorbed species, respectively. The feature at 532 eV due to the ethoxy



**Figure 7.** VEEL spectra of  $\text{C}_2\text{H}_5\text{OH}$  adsorbed on Zn(0001) surface at 80 K and progressively warmed to higher temperatures.

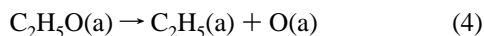
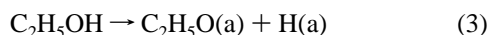
species appears at 120 K and vanishes below 225 K. The disappearance of all the features in the O(1s) spectrum at or above 225 K shows the absence of oxidic species, CO, or a carbonyl compound on the surface.

In order to confirm the results from XPS studies, we have studied the VEELS of ethanol on the Zn(0001) surface (Figure 7). The VEEL spectrum at 80 K shows a weak OH stretching band around  $3300\text{ cm}^{-1}$  in addition to features at 1090 and  $940\text{ cm}^{-1}$  due to the C—O and C—C stretching vibrations. The bending and stretching bands of  $\text{CH}_3$  and  $\text{CH}_2$  groups are at 1420 and  $2900\text{ cm}^{-1}$ , respectively. On warming the surface to 150 K, the OH stretching band disappears, leaving only the bands due to C—O,  $\text{CH}_3$ , and  $\text{CH}_2$  groups. The spectrum at 300 K has only bands due to the hydrocarbon species. The VEELS data also show no evidence for CO or a carbonyl compound. It appears that, just as in the case of methanol, ethanol undergoes



**Figure 8.** C(1s) and O(1s) spectra of 2-propanol adsorbed on a polycrystalline Zn surface. 2-Propanol was first adsorbed at 80 K and the surface progressively warmed to 400 K.

proton abstraction followed by C–O bond scission as shown below:



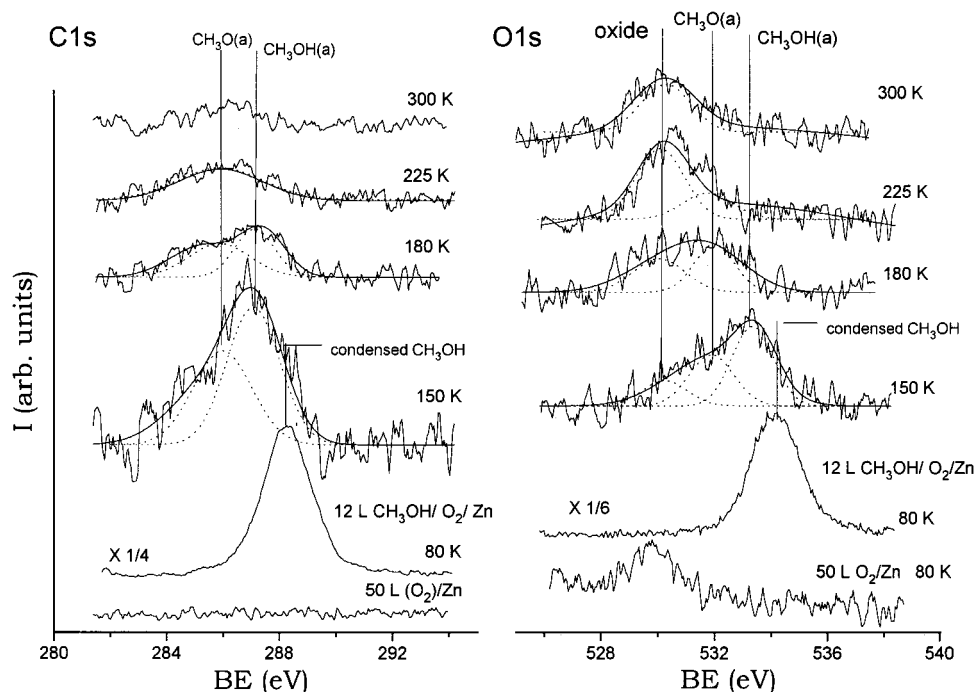
The present study does not suggest occurrence of C–C bond scission of the type reported by Cong et al.<sup>18</sup> There is also no evidence for the formation of acetaldehyde and  $\text{H}_2$  formed by the decomposition of ethanol. Again, the formation of the hydrocarbon species around 150 K is noteworthy.

**2-Propanol.** We have carried out a study of the interaction of 2-propanol with the polycrystalline Zn surface. The C(1s) and O(1s) spectra of 2-propanol adsorbed at 80 K and subsequently warmed to higher temperatures are shown in Figure 8. The C(1s) features around 288 and 286 eV at 80 K are due to the condensed alcohol and the 2-propoxy species, respectively. These binding energy values are in good agreement with those reported for 1- and 2-propanol on a Mo(110) surface.<sup>19</sup> We find no evidence for chemisorbed 2-propanol in the C(1s) and O(1s) spectra. The C(1s) feature due to the alkoxy species in Figure 8 is intense even at 80 K, in sharp contrast to that in the case of ethanol and methanol on the same surface. In the last two alcohols, the alkoxy species appears at or above 120 K. The feature around 285 eV due to the  $(\text{CH})_x$  species at 150 K in the case of 2-propanol as well. On warming to 225 K and above, the alkoxy species coexists with the  $(\text{CH})_x$  species, the latter remaining even at 400 K, though weak in intensity. Clearly, some of the hydrocarbon species desorbs from the surface before 400 K. The O(1s) spectrum shows an intense feature at 534 eV due to condensed 2-propanol at 80 K. On warming to 150 K and above, a weak feature at 532 eV due to the 2-propoxy species occurs. These binding energy values are close to those reported for 2-propanol on Mo(110).<sup>19</sup> We do not see any O(1s) feature above 300 K, indicating the absence of any oxygenated species on the surface. From the C(1s) and O(1s) spectra, we conclude that the mode of decomposition of

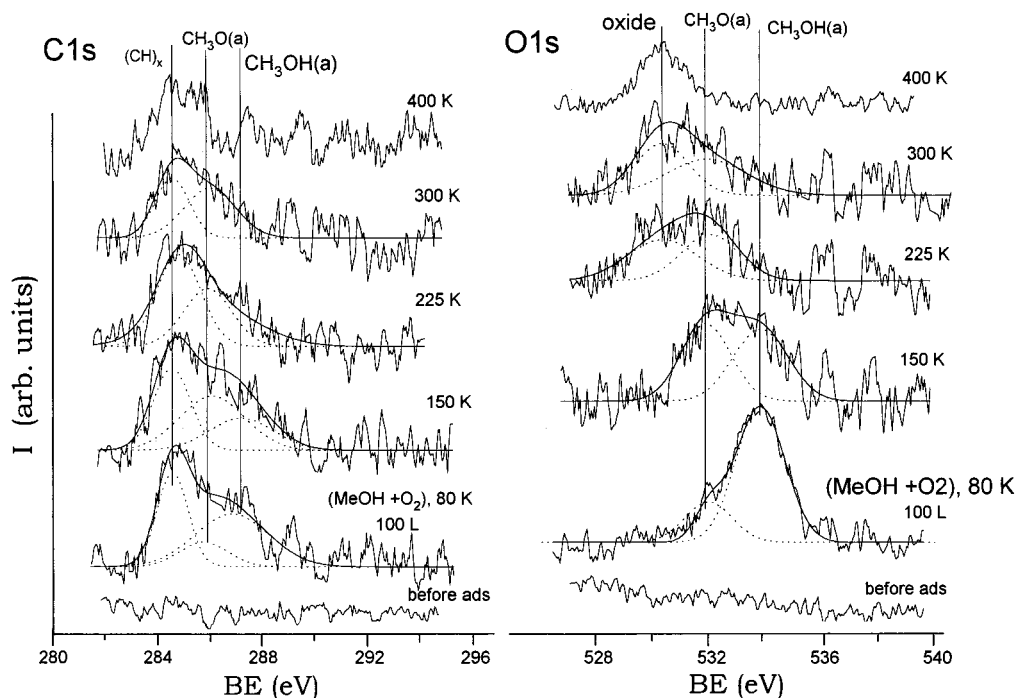
2-propanol on the Zn surface is similar to that of ethanol and methanol, but the 2-propoxy species is stable up to 300 K. C–O bond scission in the 1-propoxy species is reported to occur above 350 K on a Mo(110) surface to form propene and atomic oxygen.<sup>19</sup> The C–O bond scission on Zn occurs at 150 K, in spite of the stability of the alkoxy species.

**Effect of Predosed and Coadsorbed Oxygen.** We have examined the effect of predosed oxygen on the adsorption of methanol on the surface of polycrystalline Zn, by first exposing the clean Zn surface to 50 langmuirs of  $\text{O}_2$  at 80 K and then to methanol. The oxygen exposed surface shows the O(1s) signal at 530 eV due to atomic oxygen.<sup>26</sup> (Note that this situation is different from that in Figures 1 and 2 where oxygen is only from C–O bond scission resulting in a very small value of langmuirs). Adsorption of methanol on the oxygen-predosed zinc surface at 80 K, causes intense C(1s) and O(1s) features at 288 and 534 eV, respectively, due to the physisorbed species which desorbs at 150 K (Figure 9). At 150 K, chemisorbed methanol, with the C(1s) and O(1s) features at 287 and 533.5 eV, respectively, is found on the surface. The methoxy species also appears at this temperature with C(1s) and O(1s) features at 286 and 533.6 eV, respectively, and remains up to 225 K. There is no evidence for the formation of  $\text{CH}_x$  type species arising from C–O bond scission. The main effect of predosed oxygen is to favor the formation of the methoxy species,<sup>27</sup> but the methoxy species does not decompose further probably due to the absence of sufficient “free” Zn sites necessary for the purpose.

Adsorption of a 3:1 methanol–oxygen mixture on the polycrystalline Zn surface at 80 K gives the C(1s) feature (Figure 10) due to chemisorbed methanol at 287 eV, in addition to a weak feature due to methoxy at 285.8. More importantly, an intense feature at 284.6 due to the  $(\text{CH})_x$  type species also appears at this temperature. The feature at 284.6 eV persists up to 400 K, while the methoxy species is present up to 300 K. The O(1s) spectrum at 80 K also shows a weak feature around 532 eV due to the methoxy species in addition to the feature at 533.5 eV due to the chemisorbed species. The proportion of



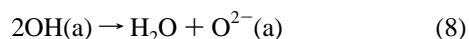
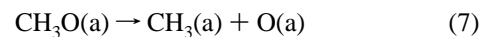
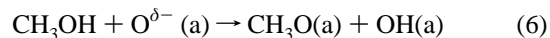
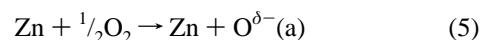
**Figure 9.** C(1s) and O(1s) spectra of CH<sub>3</sub>OH adsorbed on a polycrystalline Zn surface with prior exposure to oxygen (50 langmuirs O<sub>2</sub> at 80 K). CH<sub>3</sub>OH was first adsorbed at 80 K and the surface progressively warmed to 400 K.



**Figure 10.** C(1s) and O(1s) spectra of a 3:1 mixture of CH<sub>3</sub>OH and O<sub>2</sub> adsorbed on a polycrystalline Zn. The mixture was adsorbed at 80 K and the surface progressively warmed to 400 K.

the condensed species at 80 K, if any, is small. At 150 K, there is an increase in the intensity of the feature due to methoxy species, at the expense of the feature due to the chemisorbed species. At 225 K, there is no feature in the O(1s) as well as in the C(1s) spectra due to chemisorbed methanol. However, an O(1s) feature appears at 530 eV due to the surface oxidic species and this feature remains up to 400 K. Coadsorption of oxygen appears to give rise to a reactive O<sup>δ-</sup> type of species on the surface. It is known from the literature<sup>28–30</sup> that low exposures of oxygen on most transition metal surfaces at 80 K yields such transient oxygen species. The reactive oxygen species interacts with methanol to form OCH<sub>3</sub> and OH even at 80 K, the OCH<sub>3</sub>

readily transforming to CH<sub>3</sub> or (CH)<sub>x</sub> and oxygen. The sequence of transformations can be written as follows:

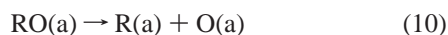


The formation of the (CH)<sub>x</sub> type species even at 80 K and oxide-like species at higher temperatures can be understood in the

light of above equations. Interaction of the reactive oxygen species with  $\text{NH}_3$  on transition metal surfaces is known to give hydroxy species which leave as water.<sup>30</sup> The occurrence of the  $\text{CH}_3$  or  $(\text{CH})_x$  type species at 80 K suggests that C–O bond scission is favored by coadsorption of oxygen with methanol.

### Conclusions

The present study on the interaction of methanol, ethanol, and 2-propanol with Zn surfaces reveals that hydrogen abstraction occurs first to give the alkoxy species, followed by the scission of the C–O bond, forming the hydrocarbon species.



In the case of methanol, there is not much difference between polycrystalline and single-crystal surfaces. In the case of ethanol, however, the C–O bond scission seems to occur at a lower temperature on the polycrystalline Zn surface. On the polycrystalline surface, the alkoxy species is most stable in the case of 2-propanol, giving rise to the 2-propoxy species even at 80 K. Predosed  $\text{O}_2$  favors the formation of the alkoxy species, but does not allow C–O bond scission. Coadsorption of methanol and oxygen, on the other hand, favors the formation of the methoxy species as well as the hydrocarbon species at very low temperatures. The occurrence of C–O bond scission of alcohols on Zn surfaces at low temperatures is noteworthy, considering that such scission occurs only at high temperatures on other metal surfaces. The mechanism of decomposition of methanol on aluminum (100)<sup>11</sup> may be relevant to the zinc surface as well.

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