Role of oxygen transients in the facile scission of C–O bonds of alcohols on Zn surfaces

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Received (in Cambridge, UK) 19th October 1998, Accepted 23rd December 1998

The alkoxy species produced by the interaction of alcohols with Zn surfaces undergoes C–O bond scission at 150 K giving hydrocarbon species, but this transformation occurs even at 80 K when alcohol–oxygen mixtures are coadsorbed, due to the oxygen transients.

Studies of the decomposition of methanol on transition metal surfaces have shown that the methoxy species formed around 150 K, undergoes C–O bond scission on some of the surfaces at relatively high temperatures giving hydrocarbon species.[1–4] Ethanol transforms to the alkoxy species on transition metal surfaces and undergoes C–O or C–C bond scission depending on the surface.[5,6] Interaction of propan-2-ol with transition metal surfaces also produces the alkoxy species and the C–O bond scission occurs at high temperatures on some of the surfaces yielding hydrocarbon species.[5,7] We have investigated the interaction of methanol on polycrystalline as well as (0001) Zn surfaces by electron spectroscopic techniques and found that the methoxy species produced around 120 K undergoes C–O bond scission at 150 K and above, giving rise to hydrocarbon species. We show the C(1s) and O(1s) spectra of methanol on a Zn(0001) surface in Fig. 1(a) and (b) respectively to illustrate the transformations. The C(1s) features due to the methoxy and hydrocarbon species are seen at 286 and 285 eV respectively at 150 K. The O(1s) spectrum shows a feature due to the methoxy species at 532 eV which disappears above 150 K. The alkoxy species formed initially undergoes C–O bond scission on the Zn(0001) surface in the cases of both ethanol and propan-2-ol. The stability of the alkoxy species increases from methanol to propan-2-ol, the alkoxy species being formed in the latter even at 80 K. Thus, in all the three alcohols, hydrogen abstraction occurs to give the alkoxy species, followed by the scission of the C–O bond forming the hydrocarbon species at 150 K. These changes are corroborated by vibrational energy loss spectroscopy. The above transformations of alcohols (ROH, R = alkyl group) on the Zn(0001) surface can be represented as follows:

$$\mathrm{ROH(a)} \rightarrow \mathrm{RO(a)} + \mathrm{H(a)} \quad (1)$$

$$\mathrm{RO(a)} \rightarrow \mathrm{R(a)} + \mathrm{O(a)} \quad (2)$$

We were interested in examining the effect of $O^{\delta-}$ type reactive oxygen transients on the interaction of alcohols with the Zn(0001) surface, since such species are known to readily abstract hydrogen from NH_3 and other molecules.[8,9] For this purpose, we have investigated the coadsorption of a 3 : 1 mixture of methanol and oxygen on the Zn(0001) surface. Typical C(1s) and O(1s) spectra are shown in Fig. 1(c) and (d) respectively. In the C(1s) spectrum, the feature due the methoxy species at 286 eV appears at 80 K, along with a weak feature at 287 eV due to chemisorbed methanol. More importantly, a relatively intense feature due to the hydrocarbon species with a C(1s) binding energy around 285 eV also occurs at 80 K. The O(1s) spectrum shows the presence of chemisorbed methanol and the methoxy species at 80 K with O(1s) binding energies at 533.6 eV and 532 eV respectively. A feature around 530 eV due to the oxidic species emerges progressively with increasing temperature. Coadsorption of oxygen with methanol appears to give rise to the short-lived reactive $O^{\delta-}$ type of transient species which readily abstracts hydrogen from methanol even at 80 K, the OCH_3 species subsequently giving the $(CH)_x$ species through C–O bond scission. It should be noted that the coadsorption of methanol and oxygen on a Cu(110) surface only yields OCH_3 and formate[10]

Coadsorption of a 3 : 1 mixture of ethanol and oxygen on the Zn(0001) surface also results in the formation of the alkoxy and the hydrocarbon species at 80 K, with a progressive increase in the hydrocarbon species with increase in temperature. In Fig. 2(a) we show typical C(1s) spectra to illustrate the transformations. Coadsorption of a 3 : 1 mixture of propan-2-ol and oxygen on the Zn(0001) surface gives a high proportion of the hydrocarbon species at 80 K as can be seen from Fig. 2(b). It should be recalled that amongst the three alcohols studied, the proportion of the alkoxy species formed on Zn surfaces is highest in the case of propan-2-ol. Since the formation of the alkoxy species precedes the C–O bond scission, the ease of

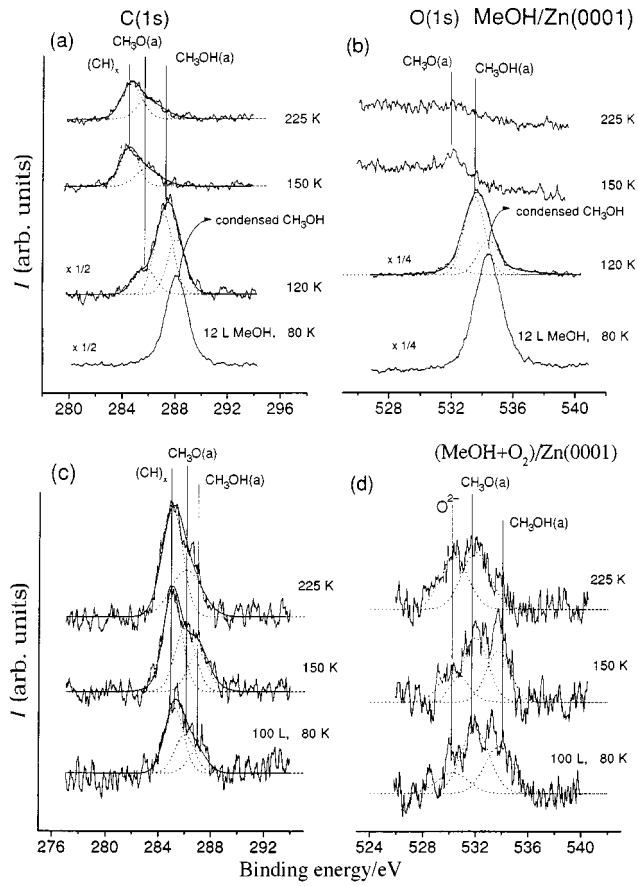

Fig. 1 (a) C(1s) and (b) O(1s) spectra of CH_3OH adsorbed on a Zn(0001) surface. CH_3OH was first adsorbed at 80 K and the surface progressively warmed to 225 K. (c) C(1s) and (d) O(1s) spectra of a 3 : 1 mixture of CH_3OH and O_2 adsorbed on Zn(0001). The mixture was adsorbed at 80 K and the surface progressively warmed to 225 K.

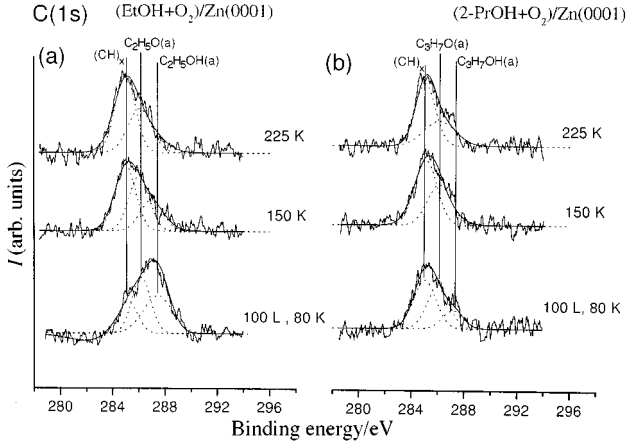

Fig. 2 C(1s) spectra of (a) of a 3 : 1 mixture of C_2H_5OH and O_2 and (b) of a 3 : 1 mixture of propan-2-ol and O_2 adsorbed on a Zn(0001) surface. The alcohol–oxygen mixture was adsorbed at 80 K and the surface progressively warmed to 225 K.

formation of the hydrocarbons will be related to the abundance of the alkoxy species. It is known that adsorption of alcohols on ZnO surfaces gives rise to alkenes, aldehydes and ketones.[11] However, in the present study on Zn surfaces, we only observe the formation of hydrocarbons.

The formation of the $(CH)_x$ type species at 80 K by the interaction of alcohol–oxygen mixtures with Zn surfaces suggests that the C–O bond scission is favoured by the oxygen transient. We represent these transformations as follows:

$$Zn + 1/2O_2 \rightarrow Zn + O^{\delta-}(a) \quad (3)$$

$$ROH + O^{\delta-}(a) \rightarrow RO(a) + OH(a) \quad (4)$$

$$RO(a) \rightarrow R(a) + O(a) \quad (5)$$

$$2OH(a) \rightarrow H_2O + O^{2-}(a) \quad (6)$$

We consider the occurrence of C–O bond scission in alcohols at as low a temperature as 80 K to be significant, considering that such scission occurs at 150 K in the absence of oxygen on the Zn(0001) surface and at much higher temperatures on other transition metal surfaces.

Notes and references

1 R. J. Levis, J. Zhicheng and N. Winograd, *J. Am. Chem. Soc.*, 1989, **111**, 4605.
2 M. Rebholz, V. Matolin, R. Prins and N. Kruse, *Surf. Sci.*, 1991, **251/252**, 1117.
3 J. Wang and R. I. Masel, *J. Am. Chem. Soc.*, 1991, **113**, 5850.
4 S. Chaturvedi and D. R. Strongin, *J. Phys. Chem. B*, 1998, **102**, 2970; B.-R. Sheu and D. R. Strongin, *J. Catal.*, 1995, **154**, 379.
5 M. Bowker and R. J. Madix, *Surf. Sci.*, 1982, **116**, 549; J. B. Benziger and R. J. Madix, *J. Catal.*, 1980, **65**, 36.
6 C. J. Houtman and M. A. Barteau, *J. Catal.*, 1991, **130**, 528.
7 B. C. Wiegand, P. Uvdal, J. G. Serafin and C. M. Friend, *J. Phys. Chem.*, 1992, **96**, 5063; B. C. Wiegand, P. Uvdal, J. G. Serafin and C. M. Friend, *J. Am. Chem. Soc.*, 1991, **113**, 6686.
8 M. W. Roberts, *Chem. Soc. Rev.*, 1996, 437.
9 A. F. Carley, P. R. Davies and M. W. Roberts, *Chem. Commun.*, 1998, 1793; G. U. Kulkarni, C. N. R. Rao and M. W. Roberts, *J. Phys. Chem.*, 1996, **99**, 3310; G. U. Kulkarni, C. N. R. Rao and M. W. Roberts, *Langmuir*, 1995, **11**, 2572.
10 P. R. Davies and G. G. Mariotti, *Chem. Commun.*, 1996, 2319; P. R. Davies and G. G. Mariotti, *Catal. Lett.*, 1997, **43**, 261.
11 M. Bowker, R. W. Petts and K. C. Waugh, *J. Catal.*, 1986, **99**, 53 and references therein.

Communication 8/08076C