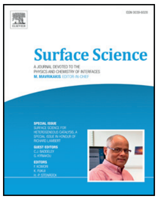
Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc



From surface science to catalysis: The importance of methoxy and formate species on Cu single crystals and industrial catalysts

M. Bowker [a,b,*], K.C. Waugh [c]

[a] Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK
[b] UK Catalysis Hub, Research Complex at Harwell (RCaH), Rutherford Appleton Laboratory, Harwell, Oxon OX11 0FA, UK
[c] School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

ARTICLE INFO

Article history:
Received 8 October 2015
Received in revised form 30 December 2015
Accepted 2 January 2016
Available online xxxx

Keywords:
Methanol oxidation
Methanol synthesis
Methoxy
Formate
Copper catalysts
Iron molybdate catalysts

ABSTRACT

Early work from the Madix group identified a number of simple surface intermediate species which have proved to be of significance for industrial catalytic processes. Two of these intermediates are the methoxy and formate surface species. We discuss the formation and behavior of these on copper surfaces, and go on to highlight their role in two important industrial reactions, namely methanol synthesis and the selective oxidation of methanol to formaldehyde. The formate is the pivotal intermediate for methanol synthesis and is formed from the reaction of CO_2 and H_2, whereas it is important to avoid the formation of that intermediate for selective methanol oxidation, which proceeds through dehydrogenation of the methoxy species.

1. Introduction

An important factor in much of catalysis is the nature and stability of a range of simple surface intermediates, which are involved in the pathway between reactants and products. A pioneer in identifying such intermediates was Bob Madix, then at Stanford University. He utilised temperature programmed methods and surface spectroscopy to identify such species on well-defined, single crystal surfaces. Especially relevant to the current paper is his work on IB metals, particularly copper, where stable methoxy (CH_3O-) and formate ($HCOO-$) species were identified by TPD and spectroscopy after the adsorption of their parent molecules [1–10].

This work and these species are relevant to a number of important industrial processes, two of which will be highlighted here, namely methanol synthesis from CO_2 and H_2 and methanol oxidation to formaldehyde. The former is carried out on Cu-based catalysts [11], while the latter now uses Ag [12] or ferric molybdate [13] catalysts. As shown below, the formate on Cu is a pivotal intermediate in methanol synthesis and both the methoxy and formate are important in the oxidation to formaldehyde.

The objective of this paper then, is to highlight the importance of Madix's findings to surface science and catalysis, and to justify that significance in relation to the latter using studies on real catalysts in the form of powdered nanomaterials.

2. Surface intermediates on Cu(110)

2.1. The methoxy intermediate on Cu(110)

The first work in this direction was in 1978 [3]. Here it was shown that there was little reactivity of the clean surface with methanol, but the surface became active when oxygen atoms were adsorbed on the surface by exposing it to molecular oxygen. Unlike Cu(111), for instance [14] oxygen adsorbs well on Cu(110) with only a small activation barrier and a sticking probability of about 0.2 at 300 K [15]. The crucial experiments were carried out by dosing labeled O^{18} onto the surface, followed by CH_3OD to distinguish hydrogen sourced from the methyl group and hydroxyl groups [3]. Fig. 1 shows part of the desorption spectrum, the label is evolved from the surface as D_2O^{18} at low temperature, releasing all the label formed by reaction and leaving a methoxy intermediate on the surface. The fact that this is an intermediate is revealed by the coincident evolution of formaldehyde, molecular hydrogen and unlabeled methanol at 370 K.

The evolution is rate-limited by the methoxy decomposition, since all the products are much more weakly bound on the surface than the

---

[*] Corresponding author at: Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK. URL: http://www.cardiff.ac.uk/chemy/contactsandpeople/academicstaff/bowker-michael-overview_new.html
E-mail address: bowkerm@cardiff.ac.uk (M. Bowker).

http://dx.doi.org/10.1016/j.susc.2016.01.001
0039-6028/© 2016 Elsevier B.V. All rights reserved.

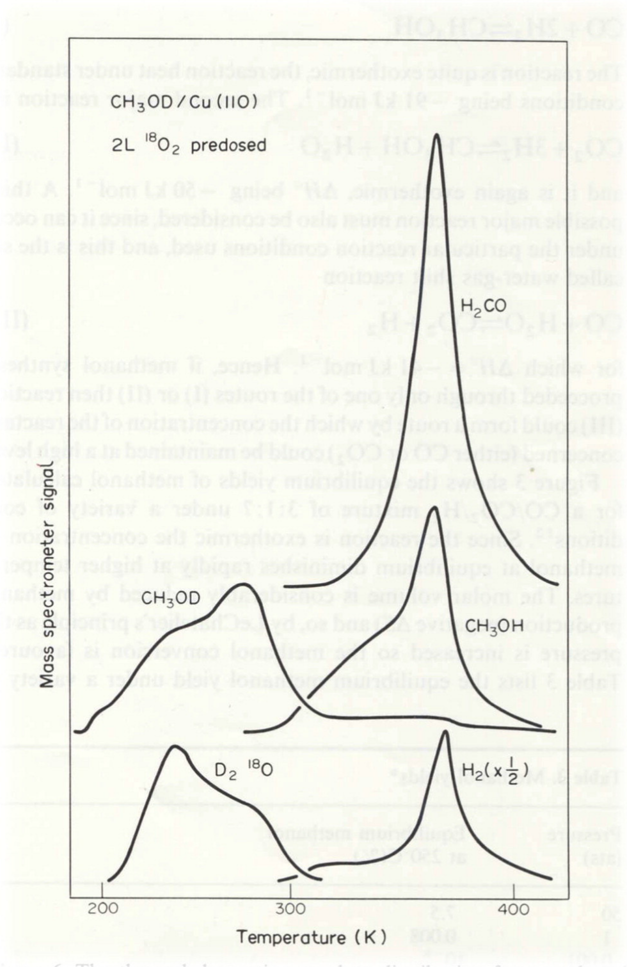


Fig. 1. Methanol reaction with adsorbed oxygen on Cu(110), showing part of the desorption revealing the presence of a methoxy intermediate on the surface by the coincident product desorption at 370 K. Adapted from Ref. [3].

intermediate itself. So a mechanism for the reaction between adsorbed oxygen and methanol was written as follows:

$CH_3OD + O_a \rightarrow CH_3O_a + OD_a$

$CH_3OD + OD_a \rightarrow CH_3O_a + D_2O$

$CH_3O_a \rightarrow CH_2O + H_a$

$2H_a \rightarrow H_2$

$CH_3O_a + H_a \rightarrow CH_3OH.$

Direct spectroscopic evidence for the methoxy was then obtained by UPS [5], Fig. 2. Here the increased symmetry of the methoxy (C_{3V}) is reflected in the spectra because the two non-bonding O_{2p} orbitals (2a″, 7a′), which are split by the H atom on the hydroxyl in methanol, become degenerate when that hydrogen atom is lost. The same applies to another pair, the 1a″/6a′ and 5a′. Further studies using FTRAIRS [16] showed the presence of the methoxy and loss of the O–H bond from the molecule.

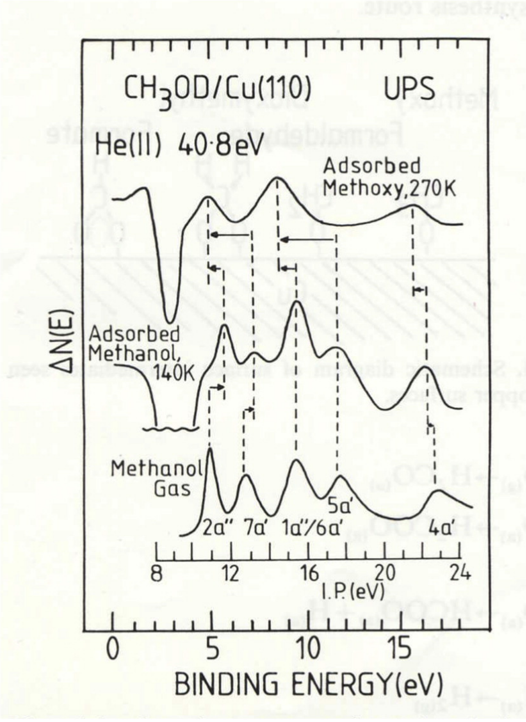


Fig. 2. UPS spectra of methanol adsorbed on clean Cu(110) at low temperature, compared with the gas phase spectrum, and that of the methoxy, showing the increased symmetry of the methoxy intermediate. From Ref. [7].

More detailed kinetic information about the reaction was obtained using a molecular beam reactor [17–19], Fig. 3. The advantage of such a reactor is that it is not limited by the need to adsorb at low temperatures where the intermediates involved are stable. Here it can be seen that the mechanism of the reaction changes between the low temperatures typical of TPD experiments, at which the methoxy is stable, and higher temperatures where is has a short lifetime. The basic difference is that at low temperature the mechanism is as shown above, which results in an overall reaction stoichiometry as below.

$$2CH_3OD + O_a \rightarrow 2H_2CO + H_2 + D_2O \qquad (1)$$

whereas the molecular beam shows that the stoichiometry changes above about 400 K approaching to the following.

$$CH_3OD + O_a \rightarrow H_2CO + HDO \qquad (2)$$

This occurs because the methoxy is unstable and it releases H atoms to the surface immediately after the hydroxyl D reacts with the adsorbed oxygen atom. HDO then forms and no molecular hydrogen is evolved. Indeed, it may be that this occurs very locally, that is, D and H add to adsorbed oxygen from the same molecule of methanol.

One fascinating aspect of this reaction is that it was known from the early days that adsorbed oxygen aided methanol adsorption and reaction (that is, methanol does not easily dissociate and yield formaldehyde on the clean surface), in effect acting as a strong base. However, it was rather strange then that increased coverages of adsorbed oxygen has a negative effect. The maximum reactivity was observed at around 0.25 monolayers coverage of oxygen atoms and reactivity was very low with 0.5 monolayers, that value being the saturation coverage of the oxygen p(2 × 1) structure. STM has provided the understanding to explain this [19–22]. It is because there is a special site for the reaction of methanol with the oxygen on the surface, which appears to be a

Please cite this article as: M. Bowker, K.C. Waugh, From surface science to catalysis: The importance of methoxy and formate species on Cu single crystals and industrial catalysts, Surf. Sci. (2016), http://dx.doi.org/10.1016/j.susc.2016.01.001