

Methanol Oxidation on Cu(110)

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Abstract. In this paper we highlight the important contribution made by Bob Madix to the understanding of catalysis at single crystal surfaces, focusing here on a favourite model system of his, namely the oxidation of methanol on Cu(110). Madix showed clearly that the methoxy was the pivotal intermediate involved, and it is bound to the surface through the oxygen atom. Here we demonstrate the nature of the reaction between methanol and oxygen at the nanoscale by STM, and further reveal that only certain oxygen atoms in the p(2x1) oxygen structure are the active sites for the reaction. These are located at the short ends of the elongated oxygen islands.

Introduction

In principle it is straightforward to analyse a simple heterogeneously catalysed reaction of the following kind:



for which the Langmuir-Hinshelwood kinetics apply, that is,

$$\text{Rate} = k[A_{(a)}][B_{(a)}]$$

where the subscripts indicate adsorbed reactants.

However, the problem is that there are at least 5 different rate constants involved (surface reaction and adsorption and desorption for reactants) in determining the coverages of reactants and these constants are often very themselves strong functions of

the coverage of both reactants. Furthermore, these coverage functions are complicated, determined by lateral interactions between species in the surface, by diffusion in the weakly held molecular states, and by surface atom rearrangements such as reconstructions which may occur as the coverage alters with changing conditions.

Thus, understanding the details of the kinetics of individual reactions in a mechanistic scheme is crucial. It is essential to achieve an understanding of such phenomena on both single crystals and catalysts. However, it is often difficult to obtain detailed, non-averaged kinetic information from the latter, hence the advantage of using the former type of substrate. Bob Madix pioneered the understanding of basic catalytic processes on single crystal surfaces [1-5]. A particularly successful example of his approach was the adsorption and reaction of methanol with copper single crystal surfaces, and this has become something of a model system for surface reactions. By the careful application of (in particular) TPD he was able to elucidate the mechanism of this reaction in individual steps, beginning with the papers by Wachs and Madix [6,7], but continuing through a series of other works using a variety of analytical methods [8,9].

Thus, we may ask ourselves, in the light of this work by Bob Madix, is there anything more to be done on this system? The answer is, yes, of course. All of the work above used macroscopic techniques which yielded no direct information regarding the nature of the structural arrangements/rearrangements occurring at the molecular scale. Madix's work on this reaction was carried out before the advent of STM, and in this paper we show that we have now added understanding of the reaction at the nanoscale, and, in particular, we have identified which sites are the most active for the reaction.

Experimental

STM experiments were performed using a WA Technology variable temperature STM partly based on the design of the FOM Institute [10], which has been described in detail elsewhere [11]. The STM was contained within a UHV chamber equipped with additional facilities for Ar⁺ ion sputtering, low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Both LEED and AES measurements were carried

out using a three-grid retarding field analyser with integral electron gun. Temperature programmed desorption (TPD) and residual gas analysis were performed using a quadrupole mass spectrometer. The chamber was ion pumped to produce a typical base pressure of 1×10^{-10} mbar while additional pumping for high gas loads, during sputtering and the initial stages of bakeout, was available from a turbomolecular pump backed by a rotary pump. Gas dosing was carried out by backfilling the chamber. Using a wobble stick, the sample holder with integral heater and thermocouple could be transferred within the chamber between the STM stage and a manipulator which allowed access to the other experimental techniques. The sample was heated both radiatively and if necessary with electron bombardment using a tungsten filament situated close to the back face of the crystal. During scanning the sample was placed horizontally with the scanner above offset to one edge to allow coarse approach of the sample to the tip via a sample tilting mechanism [11].

The images reported here are raw data, except for a simple global plane subtraction. They are not filtered or manipulated in any other way. Bias voltages quoted in the figure captions are sample biases relative to the tip.

The Cu(110) sample was cleaned using cycles of Ar^+ ion bombardment (500 eV, 10 μA) at 720 K, cooling to room temperature in the ion beam and vacuum annealing to 720 K. This procedure produced a good (1×1) LEED pattern and left no detectable trace of sulphur or carbon in AES.

The molecular beam system, which has been described in detail elsewhere [12], produces a collimated beam of thermal gas molecules that can be directed at a crystal surface. For the types of experiment described in this publication it is essential to obtain a reasonable beam intensity from low vapour pressure materials, preferably with only a few mbar pressure in the gas line. The beam originates in an heatable source capillary made of quartz with an internal diameter of 0.2 mm. The beam is formed through a conical skimmer and final defining collimator and the whole is designed to produce a constant flux across the beam diameter at the sample, with a minimised penumbra of

varying intensity. This is absolutely necessary for obtaining the correct dependence of sticking probability (S) upon coverage. The in-beam pressure of gas molecules is approximately 1×10^{-7} mbar.

The reactor can be run in several modes.

- (i) Transient mode: Here one reactant is dosed first and then the other reactant is introduced in a sequential manner.
- (ii) Steady state mode: Here both reactants are in the beam simultaneously and are directed at the crystal which is held at fixed temperature.
- (iii) Temperature programmed mode: This uses either mixed beam or single species dosing while slowly ramping the crystal temperature to measure the temperature dependence of reaction probability, uptake and product evolution.
- (iv) Pseudo-steady state mode: Step jumps in temperature are employed to carry out near isothermal rate measurements relatively quickly for mixed or single species beams.

These modes have been described in more detail in an earlier review [12]. In this paper we will describe the application of STM and molecular beam techniques to a particular system, namely the reaction of methanol with Cu(110), and this uses only mode (i) above.

Results and Discussion

Methanol reacts poorly with the pure, clean copper surface, but, as shown originally by Madix [6,7], if the surface is predosed with oxygen, then the reactivity is enhanced. This is shown in fig 1 which shows the sticking probability of methanol on 0.25 monolayer of oxygen atoms dosed onto the surface. The reaction probability is

maximised at ~ 0.2 and the reaction stops when the surface is saturated with methoxy groups. The reaction has occurred between the acid hydrogen of the methanol and the very basic surface oxygen atoms, yielding methoxy groups on the surface and water in the gas phase [6,7,13-15]. Indeed if CH₃OD is used, only D₂O is produced in the gas phase [13], in parallel with some of Madix's early TPD work [6]. The reactions occurring are



Thus we have learned that methoxy is a stable surface intermediate at ambient temperature, and Madix's TPD revealed that this is the species which dehydrogenates at $\sim 370\text{K}$ to give formaldehyde in the gas phase [6,7]. It is surprising, then, in the light of these results, that when we 'saturate' the surface with oxygen (0.5 monolayers of oxygen atoms in the p(2x1) structure), the reactivity is again zero initially, as shown in fig. 1. In order to understand why this is the case we needed to apply STM to image the reaction at the atomic and molecular scale.

We have shown that only some of the oxygen atoms on the surface are reactive at any one point in time. If we take a 'static' image of the Cu(110) surface after partial reaction with methanol, we see the structures in fig 2. Here we see the p(5x2) surface structure identified in several of our publications [15-20], together with a remaining p(2x1) oxygen island. An important feature of such images is that there is complete phase separation of the methoxy and remaining oxygen islands. However, we gain even more insight into the reaction from sequences of such images. As shown in fig.3 the islands of oxygen are reacted away in a very particular manner; the islands shrink in the [001] direction only. This is because the active oxygen atoms are those located at the short end of the oxygen islands in that direction, and a schematic model of the reaction then is as shown in fig 4. The methanol reacts with the terminal oxygen in step 1 to make methoxy and hydroxyl. A second methoxy reacts with the hydroxyl to produce water, which desorbs fast into the gas phase at this temperature. This leaves a terminal

copper atom, which we have shown is unstable in this configuration, diffuses away to adjacent step sites [16], leaving a newly exposed terminal oxygen atom, which now becomes reactive, having been unreactive previously. This continues until all the oxygen is used up. Further, as was mentioned above, the reactivity of a complete 0,5 monolayer p(2x1) structure was very low, and STM has revealed why this is the case [15]. Because the (2x1) islands are complete, there are very few terminal sites, and methoxy is only identified at the step edges on the surface.

Note that we need to be very careful about making the conclusion, then, that such oxygen atoms are the sites for all reactions. When we use formic acid as reactant, because it is a stronger acid, it appears to be able to react with all of the oxygen atoms in the oxygen islands, and even has a high reaction probability with a saturated 0.5 monolayer oxygen surface [11,21,22]. Also note that although here (oxygen dosed first, followed by methanol) we never saw any sign of the over-oxidation of methanol to formate, when methanol and oxygen are co-dosed, then indeed we see formate produced in the STM images (with a characteristic c(2x2) structure) [19,20,23].

Conclusions

Bob Madix's contribution to a fundamental understanding of processes in catalysis has been pivotal. He developed and applied some of the basic tools needed to understand reactivity in a systematic way. In particular, this paper, concerns a particular system, namely, the reactivity of methanol with oxidised Cu(110) surface, something of a model system for catalysis in general. He determined the mechanism and kinetics of the reaction, showing that the methoxy species is the intermediate involved in the selective oxidation to formaldehyde and that reactivity was enormously enhanced by the presence of oxygen on the surface. In more recent times we have built on this knowledge by using STM to identify the nanoscopic details of the reaction. Most importantly this shows that the active site for methanol oxidation is the terminal oxygen atom located at the short end of the long, thin islands which generally form on Cu(110). The number of such sites is maximised near 0.25 monolayers coverage of oxygen, for which reactivity is high, but they are essentially eliminated upon completion of the

p(2x1) oxygen structure (0.5 monolayers of oxygen atoms), so the reactivity is then very low.

Acknowledgements. I am grateful to a number of bright postdocs who have been involved in this work over the years, including Fred Leibsle, Adrian Jones, Stephen Poulston and Roger Bennett

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Figure Legends

Figure 1. Molecular beam measurements of the sticking probability of methanol on two different precoverages of oxygen on the Cu(110) surface at 353K surface temperature. hydrogen, water and formaldehyde are evolved coincidentally with the sticking. Note the low initial sticking probability of the 0.5 monolayer surface.

Figure 2. STM images of the Cu(110) surface precovered with ~0.25 monolayers of oxygen atoms. Top panel, after partial reaction with gas phase methanol, showing a phase-separated layer with a co-existing island of methoxy and remaining oxygen, image size 87 x 87Å. Bottom panel, after complete reaction, showing the detailed structure of the methoxy p(5x2) glide-line structure, the rectangle shows the unit cell, 57 x 57Å.

Figure 3. Time-lapse images of a surface predosed with ~0.25 monolayers of oxygen reacting with gas phase methanol. The oxygen islands diminish from image a to f while methoxy islands grow. However, the reaction occurs in a very particular way – the oxygen island shrinks from the short ends. Image sizes a – 114 x 114Å, b-f, 85 x 85Å. The reaction was carried out with 5×10^{-9} mbar of methanol in the gas phase. The timing of the image sequence a-f is, 0, 120, 300, 480, 780, 840 seconds.

Figure 4. Schematic diagram of the reaction of methanol with the p(2x1) islands of oxygen, highlighting terminal oxygen atoms as the active sites for methanol dehydrogenation to methoxy.

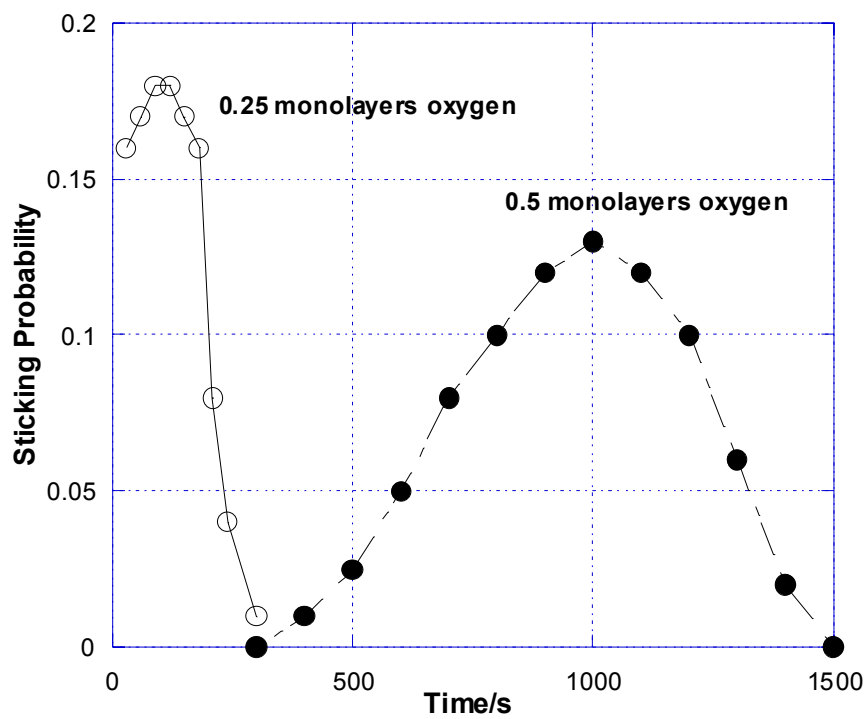
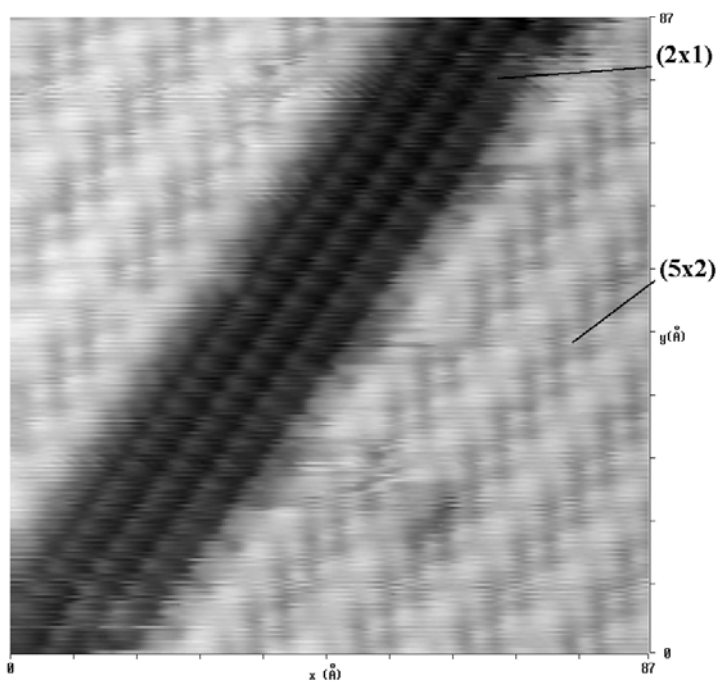


Figure 1.

Figure 2



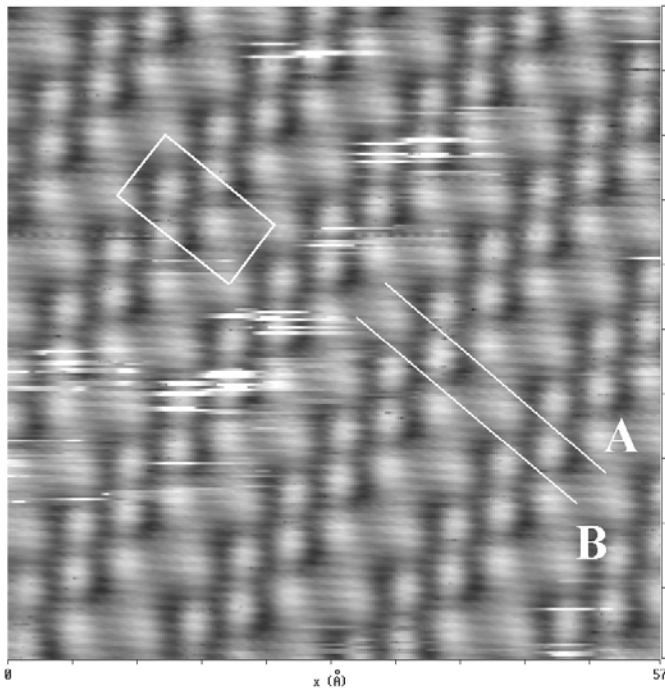


Figure 3

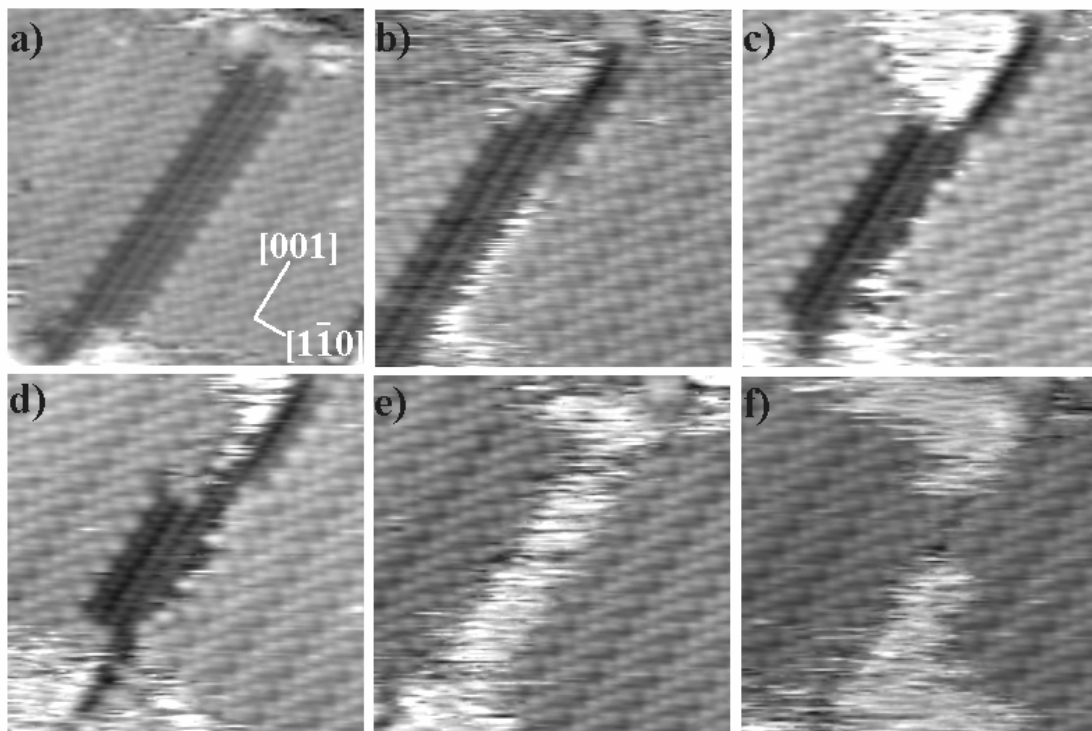


Figure 4

