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PRECURSOR STATE EFFECTS IN CATALYSIS: OXIDATIVE DEHYDROGENATION OF PROPAN-2-OL ON Cu(110)

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The oxidative dehydrogenation of propan-2-ol has been investigated using a thermal molecular beam system. The main products after predosing the surface with oxygen atoms are the dehydrogenated molecule (acetone), water and hydrogen. The effect of oxygen is to enhance the sticking of propan-2-ol from approximately 0.05 on the clean surface to 0.76 (±0.02). By varying the oxygen predose we have shown unambiguously that precursor state effects dominate the catalytic reaction, since at oxygen coverages as low as 0.008 monolayers the propanol sticking probability remains at 0.76. This is due to the long lifetime and diffusivity of the reactant on the surface enabling it to 'seek out' the active sites (those with oxygen atoms) on the surface.

1. Introduction

The existence of precursor states which might be involved in adsorption was proposed many years ago by Taylor and Langmuir [1], and a coherent kinetic scheme for the effects of such states on sticking on surfaces was described in 1957 by Kisliuk [2]. These models were derived in an attempt to describe the non-Langmuirian shape of nitrogen sticking curves obtained from adsorption studies on tungsten [3]. It was observed that the rate of adsorption was independent of adsorbate coverage over quite a wide range. The precursor model can explain this in terms of the relatively long diffusive lifetime of this state on the surface–it can weakly adsorb on filled chemisorption sites, hop from site to site over a few lattice units and finally chemisorb upon encountering a vacant site. King further showed this model to fit experimental data for adsorption on a variety of single crystal tungsten surfaces when adsorbate structure was also taken into account [4,5]; he extended the model to describe precursor effects on desorption spectra [6,7], and these effects too can be most marked.

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Although the literature on precursor effects on adsorption and desorption is now fairly extensive, there are no equivalent experimental observations of the direct role of such a phenomenon in a complex catalytic reaction. In this paper we describe just such a finding, discovered using a molecualr beam system which is capable of dosing very small amounts of oxygen onto the Cu(110) crystal surface and to distinguish the very small yields of product (but very large in terms of percent conversion) which are evolved into the gas phase.

2. Experimental

The experiments were carried out using a thermal molecular beam system (which has been described in detail elsewhere [8]), and the beam was directed onto the Cu(110) crystal mounted on a manipulator in a UHV chamber (base pressure 1×10^{-10} Torr). The beam is 3 mm diameter at the crystal surface and has an intensity of approximately 2.5×10^{13} molecules $cm^{-2}s^{-1}$ oxygen at 10 Torr source pressure. The beam flux is linearly proportional to source pressure, since the flow within the capillary which forms the source is molecular at the exit.

The method of determining the sticking probability is described elsewhere also [8]. It simply entails measuring the ratio of the number of molecules sticking on the surface divided by those reflected when the surface does not adsorb (when it is saturated, or when an inert surface blocks the beam). With reference to fig. 1, this is the ratio $(P_2'\text{-}P_1'(t)/P_2')$, where the superscript indicates correction for the

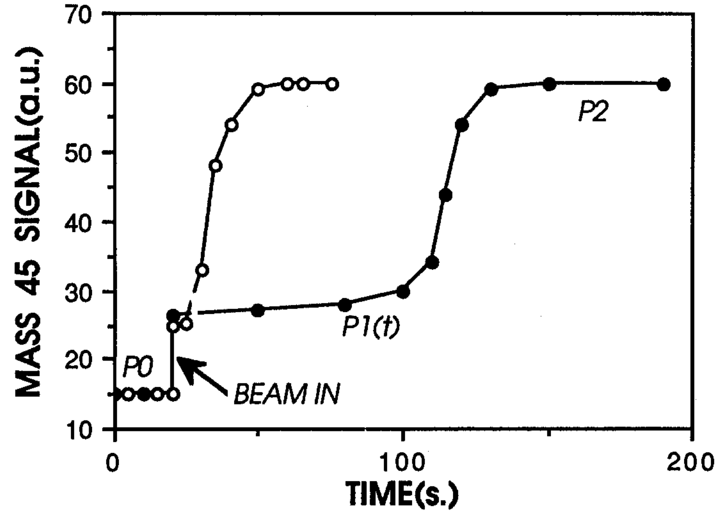

Fig. 1. Mass spectrometer signal as a function of time for propan-2-ol reaction with oxygen predosed onto the Cu(110) surface at 310 K. The arrow indicates the point in time at which the alcohol beam began to hit the surface. The data are for oxygen atom precoverages of 0.008 monolayer (yo) and 0.25 monolayer (●). Note that for the former, the beam intensity is lower by a factor of 5 and so the pressure rise has been multiplied by this factor to compare the curve with the 0.25 monolayer run. Pressure rise P_2 corresponds with reflection of all the propan-2-ol from the surface (very little reaction).

background leakage of oxygen from the beam system, P_O. The propan-2-ol pressure and products evolving from the surface were ccontinuously monitored using a Vacuum Generators Micromass PC200D in multiplexing mode. The uptake of propan-2-ol referred to later in this paper is simply determined from the time integral of the sticking probability by comparison of that with the saturation uptake of oxygen, taken to be half a monolayer of atoms. The integral is corrected for the beam intensity difference for the two species arising from their different molecular masses.

The cleanliness of the Cu(110) surface was verified by Auger electron spectroscopy and by measuring the initial sticking coefficient for oxygen at 310 K (0.21, [8,9]). Its structure was checked by LEED. The surface was cleaned before experiments by Ar ion sputtering at a current of 4 μA for 30 minutes at 600 K. The experiments shown in figs. 1-3 were all carried out a crystal temperature of 310 K.

3. Results and discussion

The reaction between propan-2-ol in the beam and a patch of predosed oxygen has been studied in detail and will be reported elsewhere [10], together with results from ethanol and propan-1-ol. Data for the oxidative dehydrogenation of methanol using the molecular beam system have already appeared [8,9]. The point of the present paper is to illustrate a newly observed effect in such catalytic reactions, namely the demonstration of the important role that precursor states can play in maintaining reaction rates high when there is a very low coverage of one reactant. Thus fig. 1 shows two sets of data taken at the extremes of our coverage range of adsorbed atomic oxygen and at a crystal temperature of 310 K; only two sets are shown for clarity, though many more were taken at intermediate coverages. In order to accurately dose very small amounts of oxygen, we had to reduce our beam source pressure to 0.1 of the normal value (which is 10 Torr), and to expose the surface to the beam for only three seconds (in the case of the smallest dose of gas). To saturate the copper surface with the oxygen $p(2 \times 1)$ structure ($\frac{1}{2}$ monolayer coverage with respect to the number of top layer Cu atoms on the clean surface) requires about 200 seconds at normal source pressures. Similarly, in order to have a reasonable time to monitor the initial region of reactant sticking and product evolution, the propan-2-ol source pressure was reduced to $\frac{1}{5}$ of its normal value for the low oxygen predose curve of fig. 1. The oxidative dehydrogenation of the alcohol was also observed at steady state under these conditions by using a mixed beam of oxygen and propan-2-ol, but the work concentrated on the non-steady state beam work, since adsorption and reaction probabilities could be more accurately determined by that method.

The most important feature of the two sets of data, and of those for coverages in between, is the apparent invariance of the zero propanol coverage sticking

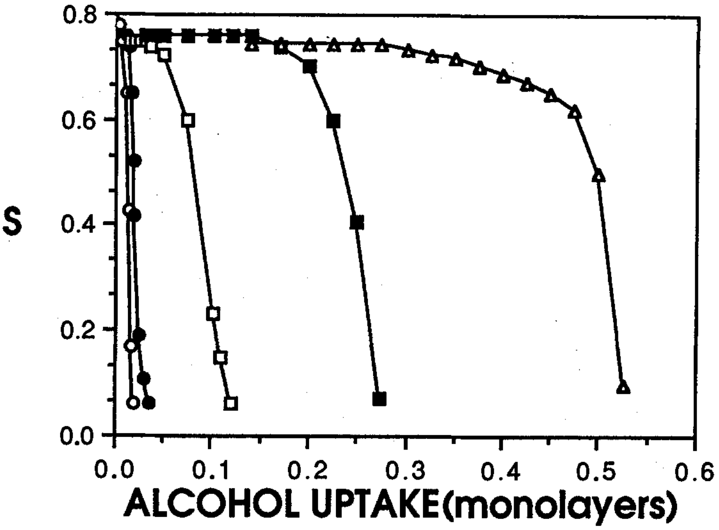

Fig. 2. Sticking probability versus propan-2-ol uptake curves derived from the types of data shown in fig. 1. The curves are for oxygen atom precoverages of 0.25 monolayer (Δ), 0.12 monolayer (■), 0.06 monolayer (□), 0.015 monolayer (●), 0.008 monolayer (○), and are for a crystal temperature of 310 K. Here 'uptake' refers to the total amount of propan-2-ol which as adsorbed and does not mean 'coverage', since the alcohol decomposes to yield acetone into the gas phase (see fig. 3).

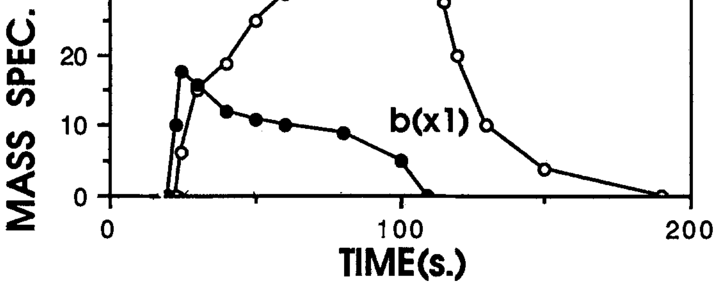

Fig. 3. Product evolution curves for propan-2-ol reaction with oxygen atom precoverages of (a) 0.008 monolayers and (b) 0.25 monolayer at a temperature of 310 K. Note that the signals for curves (a) are multiplied by a factor of two relative to 9b) and that the propanol beam intensity for the former was 0.2 of that for the latter. The mass followed for acetone evolution is 43 a.m.u. (○) and for water evolution is 18 a.m.u. (●). The component of the 43 signal due to propan-2-ol has been already subtracted from the raw data, and the data for the two coverages are offset vertically from one another for clarity.

probability (S_0) for propan-2-ol adsorption on the oxygen dosed surface. This is the case even when the oxygen predose is reduced to 0.008 of a monolayer. No oxygen dose at all results in a low value for S_0 of approximately 0.05. The sticking probability dependence on propan-2-ol uptake (referred to the clean surface atom density as one monolayer) is shown in fig. 2 for several precoverages of oxygen. Figure 3 shows the product evolution curves for the two sets of data given in fig. 1. Water and acetone are the main products, hydrogen is also evolved, but could not be followed due to the relatively high background hydrogen pressure in the UHV system (80% of the background gas is H_2). Deuterium labelling studies with other alcohols has shown H_2 evolution coincident with the dehydrogenated product [9,10].

The sticking data clearly show that propan-2-ol in a 'precursor' state is intimately involved in this reaction and that even with a coverage of only 1.5% of oxygen saturation coverage, these molecules can 'seek out' the active oxygen sites and react with them. If the oxygen adsorption were completely random at this coverage then the nearest neighbour spacing of oxygen atoms would be about 12 lattice units and so the mean distance neeeded for diffusion by the propanol from point of impact with the surface is approximately 10 Ångstroms or 4 lattice units. However, assuming a random walk diffusion (for the two fold symmetric (110) the diffusion rates might be asymmetric), the number of random diffusional transitions needed is the square of the number of hops in the straight line direction, that is, around 16 on average for each propanol molecule. This number is for the lowest precoverage of oxygen we measured. It may have been possible to go even lower in coverage and still measure a high S_0, although judging from the shape of the sticking curve (fig. 2), as soon as the average interatomic spacing gets a little bigger (soon after the exposure to propanol) the sticking coefficient begins to diminish in contrast to the higher oxygen coverages which show a plateau of cosntant sticking probability at the start of reaction.

In fact recent studies using Scanning Tunnelling Microscopy have shown that even at a coverage of < 0.01 on the Cu(110) surface the oxygen still manages to form chains on the surface as long as 50 Å in the $\langle 001 \rangle$ direction [11]. If this is still the case at the lowest coverage shown above, then the distance the precursor propanol would have to travel would be much larger than described above and could be as large as 60 lattice units.

The question arises as to the nature of this 'precursor' species. Often this is assumed to be a physisorbed entity, but the real definition is that it can be any intermediate species (intermediate to the process of final sticking, that is into a long lifetime state), which has weaker binding and a short lifetime with respect to the experimental measuring timescale; thus, it need not be a physisorbed molecule. If we use the following simple expression relating lifetimes for desorption and diffusion to determine the likely number of diffusional site hops the precursor state may make, then

$$x/a = \sqrt{n} = (Vm/Vd)^{1/2} \exp[[(Ed\text{-}Em)/2RT], \qquad (1)$$

where x is the root mean square lateral distance diffused and a is the intersite hopping distance.

If we use typical physisorption parameters and further assume that the pre-exponential ratio, Vm/Vd, is near unity, then the number of hops, n, such a species can make on the surface is about 10^5 (Ed is assumed to be 45 kJ mol^{-1} equal to the heat of vaporisation [12], Em is assumed to be $\frac{1}{3}$ of this value). The chemisorbed molecule is only slightly more strongly held than this at about 60 kJ mol^{-1} (desorption peak at 220 K versus 170 K for the physisorbed state [13]) and executes a larger number of diffusive hops across the surface, that is, about 10^8. Thus, in this case we cannot distinguish which of these may be the precursor; both can travel long distances across the surface on the timescale of our experimental data. If it were the physisorbed species that was the precursor this implies that the oxygen site, as well as being a reactive centre, enhances transition into the chemisorbed state. The fact that, for the lowest oxygen precoverage, S_0 is still as high as for the higher oxygen doses, implies that around 95% or more (assuming we could measure a drop in S_0 of greater than 5% on an individual measurement, in fact we can measure a bit better than that) of the propanol diffuses the required distance (60 lattice units, less if more randomly arranged). This in turn implies that the mean lateral diffusion distance is at least 250 lattice units, that is n is about 6×10^4 at minimum. Since S begins to diminish very quickly after the first, short plateau (fig. 2) for the lowest coverage curve, then these numbers probably approximate fairly close to the diffusivity of the propanol molecules. Considering the approximations involved, this seems fairly close to the figure for the physisorbed layer calculated from eq. (1), but very much lower than for the chemisorbed propanol. Thus, it seems more likely that the precursor state is indeed the physisorbed alcohol.

In terms of catalytic kinetics it is apparent from the data above that such a system is likely to appear unusual in the sense that, even if propanol in the precursor state were in the chemisorbed state, the rate of product formation will not follow the Langmuirian form shown below (eq. (2)). A mechanistic scheme for the reaction is shown as follows, considering that (i) the rate limiting step is (B) (that (D) is

$$R_{H_2O} = k_R \theta_{PR} \theta_o \tag{2}$$

$$C_3H_7OH \qquad C_3H_7OH_{(p)} \tag{A}$$

$$C_3H_7OH_{(p)} + O_{(a)} \qquad OH_{(a)} + C_3H_7O_{(a)} \tag{B}$$

$$C_3H_7OH_{(p)} + OH_{(a)} \qquad C_3H_7O_{(a)} + H_2O \tag{C}$$

$$C_3H_7O_{(a)} \qquad C_3H_6O + H_{(a)} \tag{D}$$

$$2H_{(a)} \qquad H_2 \tag{E}$$

relatively fast is indicated by the fact that water is evolved immediately); (ii) step (A) is at equilibrium (the low steady state coverage for such a physisorption will be achieved very quickly). The subscripts (p) and (a) refer to physisorbed and chemisorbed species, respectively. The experimental results clearly show zero order dependence on oxygen coverage over most of the range and since θ_{PR} is very low its coverage will be directly proportional to pressure. Thus, the form of the rate equation under these conditions is

$$R_{H_2O} = kP_{PR} \qquad (3)$$

where k is a product of k_R and the absorption equilibrium constant. It is clear from fig. 3 that at 310 K the acetone evolution begins relatively slowly, whereas water production is fast; both evolve coincidently above 350 K, and so $R_{H_2O} = R_{acetone}$ and the precursor effect is still shown at this temperature. Equation (3) is clearly even simpler than the Rideal-Eley reaction form [14], but the fact that the rate is proportional here to pressure is not an indication that the reaction is of the Rideal-Eley type, since under those circumstances the rate constant would simply be k_R and the rate would increase with temperature. We find the opposite behaviour (S, which is proportional to R_{H_2O}, decreases to around 0.45 at 573 K) indicating an apparent activation energy of -3kJ mol^{-1} confirming a rate constant of the form above for reaction between weakly adsorbed, diffusing propanol and strongly adsorbed oxygen–essentially a Langmuir-Hinshelwood type reaction, but with very different kinetics. k above contains an exponential term which contains the sum of reaction activation energy and heat of adsorption of the weakly held propanol ($E_r + \Delta H_p$). Assuming it is the physisorbed layer of propanol which is involved ($\Delta H = -45$ kJ mol^{-1}) then the reaction activation energy is approximately 40 kJ mol^{-1}.

It is likely that this kind of precursor effect is quite widespread in catalytic reactions, but is mainly going to be governed by (i) the type of reaction and more especially its temperature of operation and (ii) the molecular weight of the reactant. Factor (ii) here is crucial since it directly affects eq. (1) and therefore the effective range of the precursor, because (Ed-Em) is related to the molecular weight of the physisorbing molecule. Methanol, for instance, due to its smaller heat of vaporisation has a much shorter lifetime on the surface at 300 K and so visits approximately a hundredfold fewer sites during residence, but this is still around 10^3 diffusive hops. In fact, for methanol the sticking coefficient is much higher with $\frac{1}{4}$ monolayer of oxygen atoms than on the clean surface (0.6 versus θ), but drops very quickly with increasing coverage [9], in contrast to propanol.

Of course, most catalytic reactions take place at more elevated temperatures, many at around 500 K. At these temperatures the mean lifetime drops, so that for methanol at that temperature the mean lateral hopping distance from point of impact to desorption is of the order of 11 and for more weakly adsorbed, non polar molecules, can be limited to only a couple of lattice units. For the case of propan-2-ol however, there is still considerable lateral mobility, it can diffuse a mean lateral distance of around 40 lattice units at 500 K, thus still acting as a precursor, 'seeking out' active sites.

As stated above, precursor states have been described and observed frequently during adsorption and desorption processes at well defined surfaces. Recently Roberts and co-workers have also reported a surface reaction involving such weakly held states [15,16]; in their case this was for the reaction between ammonia and oxygen on the Zn(0001) plane. They found that ammonia could react with oxygen in a precursor state which enhanced oxygen dissociation (and surface oxidation) rates by 10^3. Another beautiful example of the role of weakly held states of CO has been described by Henry, who has observed CO to weakly adsorb on a catalyst support and then diffuse to the active metal component where it sticks [17].

In conclusion, we have shown that precursor states are actively involved in catalytic phenomena, exemplified in this case by the oxidative dehydrogenation of propan-2-ol on copper (110). Such states then strongly affect the kinetic relationships involved, simple Langmuir-Hinshelwood kinetics do not apply, even though the reaction involved is between two chemisorbed species. Although the work here relates to reactions on a well defined metal surface, the precursor states themselves (if physisorbed) are relatively structure insensitive and will exist and diffuse in a similar manner on catalyst surfaces under real industrial conditions. Furthermore, such a phenomenon is likely to be of importance in catalytic transformations on oxide surfaces where the reactivity is often determined by surface defects which can exist in low density. Precursor species, although impinging on inactive sites on the oxide, can nevertheless be converted to products by rapid hopping to the defect where the reaction takes place.

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