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Acetate formation and explosive decomposition during ethanol oxidation on Rh

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The adsorption and reaction of ethanol with the Rh(110) surface has been studied using a thermal molecular beam system and temperature programmed desorption. On the clean surface, ethanol shows a very simple dehydrogenation, producing hydrogen in the gas phase, adsorbed CO (which is desorbed by heating to 550 K) and carbon. Since in alcohol synthesis reactions it is likely that the surface will be partially oxidised, the reaction with predosed oxygen was also investigated. The reaction pathway then becomes much more complex. The main changes are (i) CH_4 and H_2O evolution during adsorption, and (ii) *Acetate* formation by oxygen insertion in the molecule. The acetate shows very unusual decomposition kinetics —a surface 'explosion' with a very narrow peak—yielding CO_2 and H_2 in the gas phase and adsorbed C. The acetate is always seen on Rh catalysts which are selective for alcohol synthesis from CO and H_2, and it is proposed that oxidic promoters such as vanadia may act to stabilise this intermediate.

Keywords: Alcohol dehydrogenation, ethanol, alcohol synthesis on Rh; surface explosion; autocatalytic decomposition; molecular beams; temperature programmed desorption

1. Introduction

Rh has been shown to be a most versatile metal for the hydrogenation of CO, having apparently only a weak ability to dissociate CO, but nevertheless being able to yield higher alcohols [1]. Of special interest is its ability to selectively synthesise ethanol when treated with oxidic promoters, vanadia for example. This paper is concerned with describing experiments carried out to examine the reverse pathway to synthesis, namely ethanol decomposition on a well defined surface of bulk Rh, the (110) plane. The work was done in this way because it utilised molecular beam techniques in an ultra-high vacuum system, conditions under which the synthesis itself is thermodynamically unfavourable. Future work will examine the forward reaction by use of a high pressure cell. Nevertheless, the reverse reaction reveals a great deal in relation to the pathway to synthesis itself and results in the formation of the reactants CO and H_2. The presence of oxygen on the surface significantly alters this reaction pathway and the intermediates which are formed.

2. Experimental

The equipment used was a special form of catalytic reactor, in many ways an ideal form, that is, a thermal molecular beam system. This can be classified as a *single collision* reactor, since a molecule in the beam only hits the surface once and is either reflected or desorbed again on the short timescale (and is detected in the mass spectrometer), or it sticks on the surface. Of course the latter can result in a reaction, in which case any products evolved are detected in the mass spectrometer. The molecular beam system has been described in detail elsewhere [2] and it produces a beam of 2×10^{13} molecules $cm^{-2}s^{-1}$ for N_2 at 10 Torr source pressure and 300 K. The absolute intensity depends on the molecule involved and can be calibrated directly in-situ. For experiments with oxygen, that gas was beamed onto the surface first and then the oxygen was removed from the dosing volume, replaced with ethanol and the experiment began upon unblocking the ethanol beam and allowing it to impinge on the surface. The reactants/products were detected on a Vacuum Generators model PC200D quadrupole mass spectrometer. Temperature programmed desorption also utilised the mass spectrometer for product detection and a heating rate of 1.5 K s^{-1} was used.

3. Results and discussion

3.1. CLEAN SURFACE

The reaction with the clean surface was very simple. The sticking probability of ethanol was 0.6 and the only product evolved was hydrogen. What was left on the surface was CO and C. This was evidenced by TPD when CO was evolved with a peak at 440 K, which compares well with its' desorption from clean Rh(110). However, C was left behind on the surface after this experiment, since subsequent heating in O_2 evolved CO from the surface. The temperature required for $C_{(a)} + O_{(a)}$ recombination to begin was around 330 K and the product was CO_2 peaking at 440 K, evolution and oxygen uptake being finished by 470 K. Furthermore, upon exposing the surface with C left (after adsorption + TPD) to the oxygen beam at 300 K, the uptake was much reduced, although the initial sticking coefficient was little affected. Similarly a subsequent experiment with ethanol after an initial run + TPD to remove CO resulted in ethanol uptake and hydrogen evolution, both reduced by a factor of 4 from the experiment on the clean surface.

Thus we can postulate a reaction mechanism from these data. The first step is 'acid' hydrogen dissociation (here subscript (a) refers to an adsorbed species):

$$C_2H_5OH \rightarrow C_2H_5O_{(a)} + H_{(a)} \tag{1}$$

followed by αC–H bond splitting to form the acetyl species

$$C_2H_5O_{(a)} \rightarrow CH_3CHO_{(a)} + H_{(a)} \tag{2}$$

$$CH_3CHO_{(a)} \rightarrow CH_3CO_{(a)} + H_{(a)} \tag{2a}$$

and then C–C bond splitting occurs followed by methyl dehydrogenation

$$CH_3CO_{(a)} \rightarrow CH_{3(a)} + CO_{(a)} \tag{3}$$

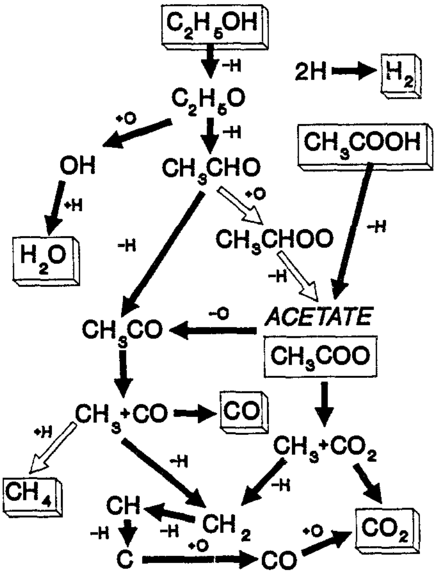
$$CH_{3(a)} \rightarrow C_{(a)} + 3H_{(a)} \tag{4}$$

and coincidently with these reactions hydrogen recombination is taking place (step 5). CO is only evolved upon heating, because it is

$$2H_{(a)} \rightarrow H_{2(g)} \tag{5}$$

relatively strongly bound on Rh. This sequence of reaction steps is

$$CO_{(a)} \rightarrow CO_{(g)} \tag{6}$$



Scheme 1. A scheme for ethanol decomposition taken from the results of this work and discussed in the text. Note that ethanol *synthesis* pathways can be inferred from the reverse of these pathways. All species are surface species, except those in 3-D boxes which are gas phase reactants or products. The unfilled arrows represent pathways only seen at high oxygen precoverages (> 0.5 monolayers). The most likely MASI, (most abundant surface intermediate), is the acetate and is shown in a 2-D box.

shown in scheme 1. The sequence of dehydrogenation is not proved in these experiments. That the ethoxy intermediate is first formed is inferred from the reaction pathway on less reactive metals such as Cu [3,4], for instance, and from the observation that the first chemisorptive contact of such molecules with the surface is via the oxygen 2p non-bonding orbitals [3]. Also experiments with deuterium labelling (C_2H_5OD) show mainly HD as a product. This is due to the fact that, at these temperatures and pressures, the ethoxy decomposes very fast and so a pool of mostly H atoms with approximately 1/5 as many D atoms is formed. By the binomial theorem then the HD evolution should be approximately 10 times that of D_2, which is in line with our observations. Once again, by analogy with Cu, the ethoxy dehydrogenates to acetaldehyde in step 2, but in contrast to IB metals, this moiety is more strongly bound and therefore does not desorb, but further dehydrogenates to acetyl in step 2a, followed by C-C scission. Further evidence for this sequence of events is given in the reaction with the oxygen dosed surface.

3.2. OXYGEN DOSED SURFACE

The adsorption of oxygen on Rh(110) has been reported in detail previously [5]. It induces considerable reconstruction in the surface, even at low coverages. The surface structure was shown to be of considerable importance for the reactivity in the CO oxidation reaction [6] and it was anticipated the same would be the case in this work. In this letter only a part of an extensive series of experiments will be described; a full description of the reactivity (and that of methanol) will be given elsewhere [7].

The most important features of the reactivity are shown in fig. 1. Here the ethanol sticks on a surface predosed with 0.65 monolayers (saturation) of oxygen atoms (relative to the number of surface atoms in Rh(110)), showing a complex pattern of product evolution; the results for C_2H_5OD are shown to clarify the reaction. The main products are water, hydrogen and methane for dosing at 310 K, there is very little CO_2. The hydrogen evolution is all mass 2, water is evolved as H_2O and HDO (approx. 3:2 ratio). A relatively strongly held intermediate is left on the surface after these reactions and this decomposes in a most unusual way as shown in fig. 2, indicate of a 'surface explosion' [8]. This is the first observation of this phenomenon on Rh. The products of this explosion depend on the amount of ethanol dosed on the surface; at high doses (> 40 s) the subsequent TPD shows coincident CO_2, H_2 evolution, while at low doses coincident evolution of CO_2 and H_2O is seen. We propose that this decomposition shows the presence of a relatively strongly held *acetate* species on the surface. This was confirmed by dosing acetic acid onto clean Rh(110) which gave the same explosive evolution of CO_2 and H_2, at a similar temperature.

The explanation of this 'explosion' in TPD is relatively simple. During a desorption profile with normal kinetics (say first order), the rate is given by the

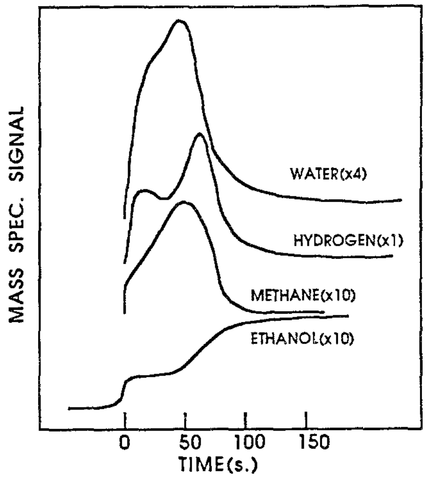


Fig. 1. Reactant and product mass spectrometer signals during the reaction of the beam of ethanol with a saturated predosed oxygen atomic layer on Rh(110) at 310 K. The beam is allowed to hit the crystal at time zero and uptake of ethanol is shown by the low reflected signal for the first 50 seconds of beaming; the surface is saturated at 100 seconds. The signals are offset vertically for clarity.

following:

$$R = \frac{d\Theta}{dt} = A\Theta \exp(-Ed/RT) \tag{I}$$

where Θ is the coverage by the decomposing intermediate, A is a first order prefactor ($\sim 10^{13}$ s^{-1}) and Ed is the decomposition activation energy. If the products formed are above their normal desorption temperature, they will evolve coincidently, rate limited by the decomposition. The important point is that the desorption rate *decreases* as the coverage goes down and acts against the exponential increase in rate given by the activation energy term; the result is a peak of ~ 24 K width for an activation energy of 100 kJ mol^{-1}, as shown in

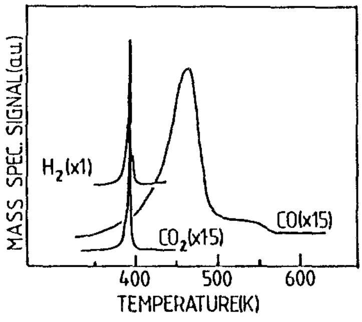


Fig. 2. TPD from the layer remaining on the surface after the beaming experiment shown if fig. 1. Note the very narrow width of the products of the explosive decomposition of the acetate at 390 K. After this desorption, carbon is left on the surface. The curves are offset vertically for clarity.

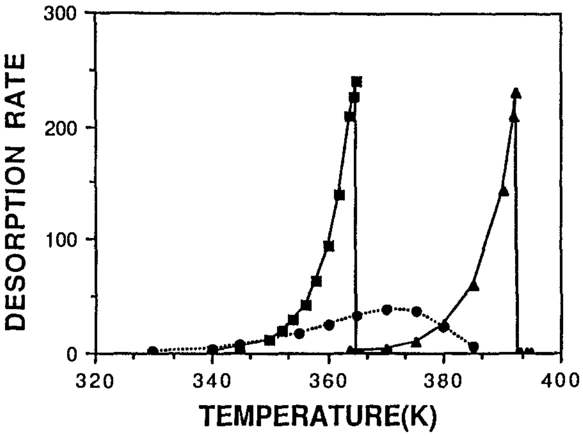


Fig. 3. Modelled desorption spectra for simple first order kinetics (●) and for the surface explosion kinetics with the initiation site coverage of 0.01 (■) and 0.0001 (▲) monolayers. The initial coverage for the three curves is unity and the other parameters are given in the text.

fig. 3. In the case of a surface explosion, however, the loss of material from the surface *enhances* the rate; there is a negative dependence on surface coverage. This can derive from a specific site requirement for decomposition. The metal surface sites are blocked by adsorbate and these are required for fast decomposition of the acetate (by some kind of frustrated rotational mode which bends the methyl group to the surface for dehydrogenation). Thus the decomposition rate depends on the number of these vacant sites. It can be considered that the decomposition begins at certain nucleation sites on the surface, perhaps steps, or defects. If there are N of these on the surface, then the decomposition rate can be approximated as follows:

$$R = k \cdot M \tag{II}$$

where k is the rate constant $(=A \exp(-Ed/RT))$ and where M is the coverage of reactive centres given by the following:

$$M = 2\pi r \frac{ND}{N_s} \tag{III}$$

r being the radius of an (assumed) circular patch of clean, reactive surface where adsorbate has already been removed by reaction, D is the density of reactive sites (cm^{-1}) at the circumference of this reactive patch and N_s is the total number of sites involved. During the TPD these reactive patches increase in radius, thus increasing the number of reactive centres (at the perimeter, the clean/adsorbate covered boundary) and hence *increasing* the rate. Thus, in essence, there is a positive feedback of temperature (or time) on rate and hence the 'explosion.' Now it is important to remove the radius term from eq. (II) and express it in terms of the experimentally determined quantity, namely the coverage of the surface by intermediates. The number of vacant sites $\Theta_v(=1-\Theta)$ is given by

$$\Theta_v = \frac{N\pi r^2}{a} \tag{IV}$$

where a is the beam area. Thus now we can substitute for r in eq. (II) from eq. (IV) showing the negative dependence on surface coverage; here $\Theta_N = N/N_s$ and represents the *coverage* of nucleation

$$\begin{aligned} R &= 2k\left(\frac{N}{N_s^2}\pi\Theta_v a\right)^{1/2} \cdot D \qquad \text{(V)} \\ &= \frac{2kD}{N_s^{1/2}}\{\Theta_N \cdot \pi \cdot a(1-\Theta)\}^{1/2} \end{aligned}$$

sites. Using the same factors in the rate constant term k as for the first order case, the result of such an explosion is shown in fig. 3. The value for Θ_N is not known accurately, although it is in the pre-exponential term and is assumed coverage independent, we have assumed that the number of these sites is small and have shown the results for two different values. The important points here are that (a) the peak is much narrower (5 K) than for the simple first order case and (b) is shifted at higher temperature (by 10 K). Note that this treatment is similar to one already given as a possibility (though dismissed in their publication) by Madix et al. [8] for the explosive decomposition of formic acid on Ni(110).

Now to return to the overall reaction mechanism on the oxidised surface. It is clear that it behaves quite differently from the clean surface. In particular, CH_4 is evolved during adsorption as is H_2O. The first stage (up to 40 s in fig. 1) evolves CH_4, H_2O and H_2 evolution at constant rate, implying initial attack by surface oxygen at the acid hydrogen of the molecule (evidenced by mainly HDO evolution for the labelled compound):

$$O_{(a)} + CH_3CH_2OD \rightarrow CH_3CH_2O_{(a)} + OD_{(a)}. \tag{7}$$

The ethoxy so formed is attacked by other adjacent oxygen atoms to give the acetate, though whether αC–H bond scission takes place before, or

$$O_{(a)} + CH_3CH_2O_{(a)} \rightarrow CH_3COO_{(a)} + 2H_{(a)} \tag{8}$$

during oxidative attack, is not clear. It may be that dehydrogenation proceeds to acetaldehyde which then undergoes nucleophilic attack by oxygen. It is clear, however, that there are no free D atoms on the surface, since subsequent recombination reactions do not evolve HD. The mobile $H_{(a)}$ species mops up long lived reactive species such as OD and other hydrogen atoms. Furthermore, since $O_{(a)}$ is in excess at the

$$OD_{(a)} + H_{(a)} \rightarrow HDO_{(a)} \rightarrow HDO_{(g)} \tag{9}$$

$$2H_{(a)} \rightarrow H_{2(g)} \tag{10}$$

start, hydrogen can also react directly with that:

$$H_{(a)} + O_{(a)} \rightarrow OH_{(a)} \tag{11}$$

$$OH_{(a)} + H_{(a)} \rightarrow H_2O_{(a)} \rightarrow H_2O_{(g)} \tag{12}$$

This explains most of the initial products, but not CH_4. It does not appear that CH_4 is derived from acetate decomposition, since CO_2 would be evolved, and it is not seen. Furthermore, acetic acid adsorption does not yield methane, but does result in acetate formation. Therefore methane must derive from another decomposition pathway involving the ethoxy or other mono-oxygenated species. In contrast to the clean surface it may be that the presence of filled sites (with O or OH) may stabilise the ethoxy (as seen for methoxy [9] and ethoxy [4] on Cu(110)), and also the methyl group, once formed. This renders the methyl group less open to dehydrogenation (clean surface reaction) and more open to the scavenging hydrogen atoms (due to its longer lifetime). Thus

$$C_2H_5O_{(a)} \rightarrow CH_{3(a)} + 2H_{(a)} + CO_{(a)} \tag{13}$$

and then

$$CH_{3(a)} + H_{(a)} \rightarrow CH_{4(g)}. \tag{14}$$

Of course, the use of a single technique is often insufficient to fully resolve a mechanism such as this and in the near future we intend to carry out reflection-adsorption infra-red spectroscopy (RAIRS) studies in order to follow the evolution and decay of surface species during the reaction.

Finally, we should consider the implications of this work for catalysis on Rh itself. The whole of the reverse synthesis is seen, especially obvious on the clean surface where H_2 and CO are seen in the gas phase, but importantly C is also present in the decomposition, and perhaps indicates the importance of the CO dissociation route to ethanol synthesis itself. It must be noted that the study of the effects of oxygen on this reaction are relevant, because CO dissociation must leave $O_{(a)}$ on the surface and also water is present during the high pressure catalysis. With oxygen the routes are more complicated, particularly with the occurrence of oxidative addition to form acetate (presumably also the precursor to acetic acid). Why CO (formed in step (13)) is not attacked by $O_{(a)}$ to yield CO_2 is not completely clear, but may again be associated with site isolation; by the time it is formed all adjacent O atoms may be OH or OD species and these presumably do not favour O–H bond breaking to make CO_2. What controls which pathway is taken by ethanol is open to speculation and it requires the use of other complementary experimental techniques to gain more information in this respect. The method we have used does not *directly* give information of the surface species present during this transient reaction and hence the need to carry out the experiments using infra-red absorption spectroscopy (in reflection mode) mentioned above.

The mechanism we have proposed can then be summarised as shown in scheme 1. It must be noted that this is broadly similar to several other schemes [10–12], especially that of Bastein et al. [12]. The latter propose that the acetate species is directly involved in ethanol synthesis (although they feel there may also be other routes), since it is always present on catalysts which synthesis ethanol (Rh/V_2O_3 [12–14], for instance) as evidenced by IR, while Rh/SiO_2, which tends to produce acetaldehyde, shows no acetate. Others feel that the acetate is a spectator (or possibly a promoter) species and is not directly involved in synthesis, which goes via an acyl entity [10,15]. Whichever is the case, the acetate is certainly the most stable surface intermediate (although CO itself is bound more strongly) and is probably the most abundant surface intermediate (MASI [16]) under synthesis conditions (as is evidenced by IR [15,17,18]). In our experiments, on the clean Rh surface, we do end up with the synthesis gas reagents CO and H_2, whereas on the oxygen treated surface large amounts of CO_2 and H_2O are formed in the gas phase. Of course water is a major product of the reaction, as is CO_2. The CO_2 is an undesirable product and in this work is shown to derive from acetate decomposition. We propose that it is the role of surface promoters, such as vanadia, to reduce the rate of combustion by preventing CO_2 formation. This occurs by the presence of strongly bound oxygen, attached to the promoter entity, which either stabilises the acetate towards decomposition, or alters its' bond breaking pathway, possibly via the acyl intermediate proposed by others [10,11,15].

The results of such a study must not be taken too far in the sense that it might be expected that very small catalyst particles would behave differently from bulk metals, due to their undeveloped band structure. However, in that respect, very small probably means < 20 Å diameter or so. It is clear from the results described above that pathways postulated by others for catalysts are seen on a single crystal surface and the acetate in particular is readily identified. The unusual autocatalytic decomposition kinetics of this intermediate (a surface explosion) are likely to be strongly structure sensitive and this will be explored more fully by the use of Rh(111) in the near future. It is also our aim to correlate the results here with high pressure cell studies of the *synthesis* reaction from CO and H_2 over the Rh(110) surface.

Acknowledgements

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