

From surface science to catalysis: surface “explosions” observed on Rh crystals and supported catalysts

T.J. Cassidy, M.D. Allen, Y. Li and M. Bowker

*Leverhulme Centre, Department of Chemistry and Surface Science Research Centre,
Liverpool University, Liverpool, L69 3BX, UK*

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Phenomena called surface “explosions” have been reported for decomposition reactions on single crystals, and have been identified by the use of desorption methods. In particular, in TPD, they are manifested by extremely narrow peaks (as little as 3 K in width) and a desorption rate which increases with time in isothermal experiments. In this paper we report such observations for acetate species on Rh single crystals, but extend this to show for the first time that such effects are not restricted to single crystal/UHV experiments, but can also be found on a Rh/Al₂O₃ catalyst under ambient pressure conditions. These reactions can be classified as second order autocatalytic surface processes, where free surface Rh sites are an essential component of the reaction. It is shown that coadsorbed adatoms are also essential for such “explosions” to be seen and their role is proposed to be that of a template layer acting to order the acetate in self-poisoning configurations.

Keywords: Surface explosions; autocatalytic reactions; acetates/Rh catalysts; temperature programmed desorption; acetic acid adsorption; acetic acid oxidation

1. Introduction

Over the last decade there has been considerable debate over the relevance of surface science studies in UHV conditions to “real” catalysis conducted at high temperature and pressure. It is now clear that surface intermediates which can be found in UHV experiments are often found to be implicated in catalysis on supported materials, a classic example of this being the early observation of stable formate species on Cu single crystals [1,2] and their later observation on catalysts during high pressure methanol synthesis [3]. Furthermore, with the addition of integral high pressure cells to UHV machines [4], the connection between these two areas of science has become more obvious.

In this paper we wish to highlight a new area of catalysis which has been accessed from UHV experiments on single crystals. Many years ago Madix et al. reported the first observations of so-called “surface explosions” on single crystal Ni(110) surfaces. These occurred for surfaces with adsorbed carboxylate species

(formate [5,6] and acetate [7]) and were manifested by an extremely narrow peak width in temperature programmed desorption (as low as 5 K full width at half maximum, compared with normal observations of ~ 30 K for desorption peaks). These observations were considered as a curiosity and possibly an anomaly in surface science circles and no one reported similar observations for such materials until the phenomenon was re-discovered at Liverpool in 1990 (published in this journal [8]), although a type of surface explosion was postulated by Fink et al. for NO coadsorbed with CO on Pt(100) [9] and was proposed to be an important component of oscillating surface reactions. The rediscovery came about from a study of ethanol oxidation on Rh(110) in UHV conditions which produced an acetate species by oxidative nucleophilic attack on the ethanol [8]. This acetate decomposed to yield CO_2 and hydrogen coincidentally into the gas phase during TPD at 390 K with a very narrow peak width (fig. 1). We subsequently went on to discover several facts about surface "explosions" by acetic acid dosing and these can be summarised as follows:

(1) An essential requirement for the observation of such autocatalytic phenomena is a coadsorbed atom. On Rh(110) explosions were observed for the acetate when coadsorbed with any atom tried (O, C and N) but acetate on the clean surface did not explode [10].

(2) It is not only observed for (110) fcc surfaces. Our initial observations were on Rh(110) and the original work of Madix was on Ni(110). Extension to Rh(111) also yielded such phenomena, although not so extreme, with peak widths as narrow as 8 K being observed [11].

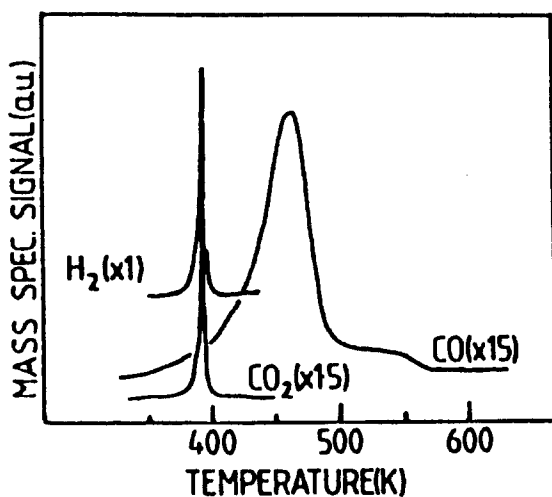


Fig. 1. Temperature programmed desorption for acetate decomposition on Rh(110) showing the sharp peak at 390 K due to the surface "explosion" [8]. This was obtained after dosing ethanol at 310 K onto the surface predosed with oxygen. Carbon was left behind on the surface after this experiment.

(3) It appears to be a general phenomenon, at least for precious metal surfaces, having now been identified also on Pd(110) [12]. It is likely that it will be seen on other surfaces also where the decomposition of the carboxylate is rate limiting in product evolution.

The reason postulated to explain the observation in item 1 above was that ordering of the acetate on the surface is essential for the explosion and that the atomic adsorbates induce such ordering. Ordering is essential because it results in active site blockage by the carboxylate itself which thus acts as a self-poison. The explosion then begins at initiation sites and proceeds outwards as a front creating more active sites at the boundary as the reaction proceeds. Descriptions of these kinds of effects have been given by Madix et al. [6] and ourselves [8] previously. A more detailed consideration of the kinetics of such processes is in preparation [13]. Such surface “explosions” are a class of autocatalytic reactions.

2. Surface explosions on Rh/Al₂O₃ catalysts

Having established, as described above, that such effects happen on more than one surface morphology and for several metals, it appeared of interest to investigate the possibility that these surface explosions would occur on a high area, supported catalyst and the sample chosen was Rh/ γ -Al₂O₃. A sample of 5% Rh/ γ -Al₂O₃ (Johnson Matthey) was used, diluted with 80% by weight of low area α -alumina ($\sim 1 \text{ m}^2 \text{ g}^{-1}$). The total metal area in the sample of 0.5 g was $\sim 1.2 \text{ m}^2$. The sample was loaded into a 1/4 inch o.d. stainless steel tube with a sheathed thermocouple present in the catalyst bed. The tube was part of a microreactor system (fig. 2), designed for transient work [14] which can be used in a pulsed flow mode. The reactor was housed in a Pye 104 temperature programmable oven. For the acetic acid dosing, the liquid was introduced directly into the system with flowing He (60 ml min^{-1}) from a syringe via a silicon/PTFE septum upstream from the catalyst bed. Small doses of only $1 \mu\text{l}$ were used. After the dose the catalyst temperature was ramped at 0.7 K s^{-1} to carry out temperature programmed desorption into the flowing He stream. Desorption could also be carried out in an isothermal fashion by heating to particular temperature and stabilising it at that value. Product detection was by mass spectrometry (VG QX200 quadrupole) run in a multiplex mode and controlled from a PC using in-house software. The mass spectrometer detected a small portion of the eluent stream by a controlled bypass flow from a pumping system. The computer also controlled six port sampling valves which allowed pulses of 0.5 ml of O₂ to be dosed onto the catalyst in a controlled fashion. When acetic acid was dosed onto the catalysts in a He flow (60 ml min^{-1}) no evidence of adsorption on the Rh component of the catalyst was found, but when O₂ was predosed then a stable intermediate was formed and upon TPD the surface “explosion” was seen (fig. 3); this was manifested by a very sharp and narrow peak of CO₂ evolution, with near coincident H₂O. These observations are very similar

to those on the single crystal surface, and represent the decomposition of the acetate species as follows:

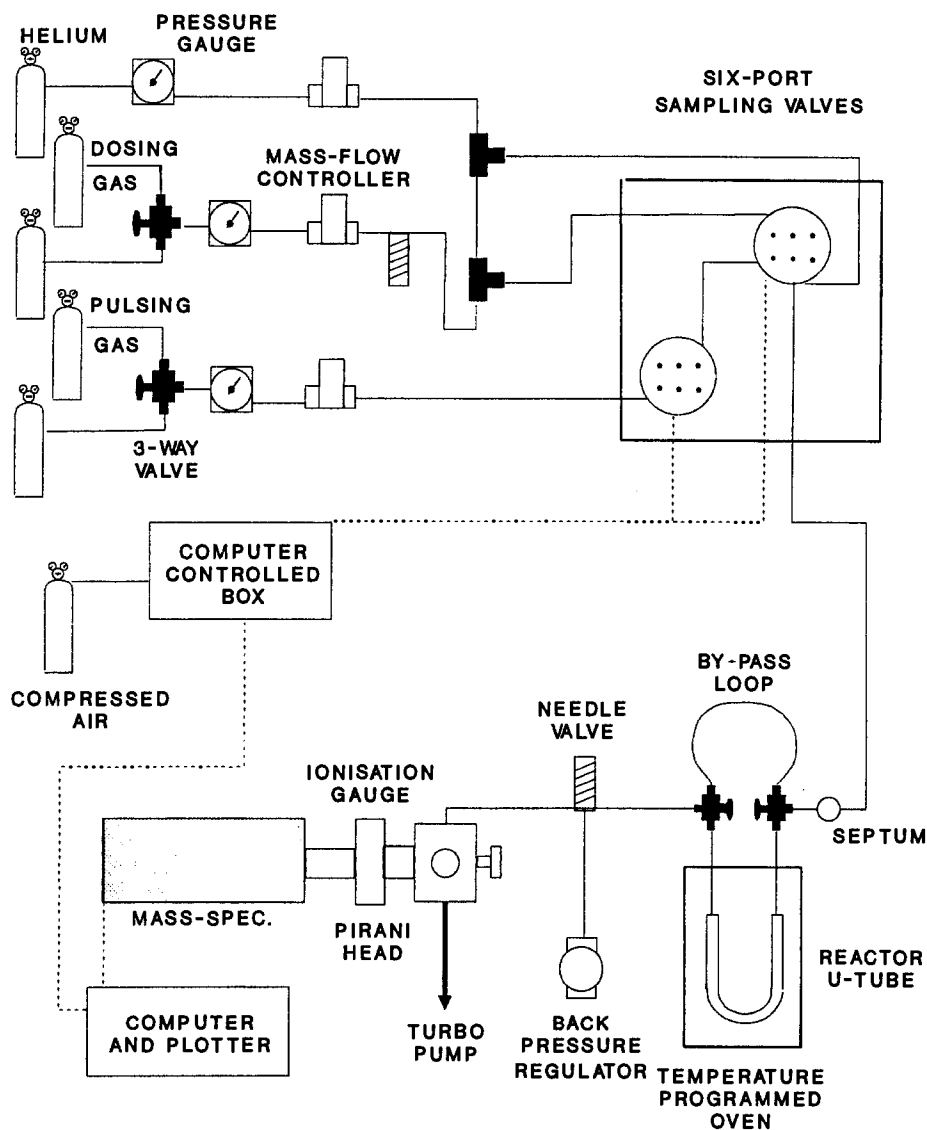
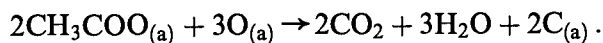


Fig. 2. Layout of the pulsed flow microreactor. The sampling valves and the mass spectrometer are computer controlled. In this work the pulsing method was not used for the acetic acid dosing, it was introduced via manual injection through a septum positioned just before the reactor oven.

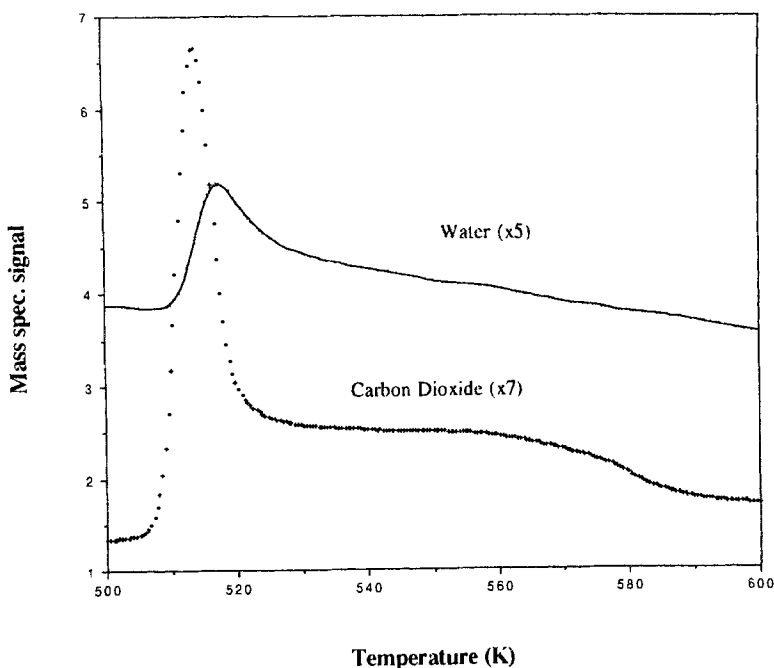


Fig. 3. Temperature programmed desorption after dosing 1 μl of acetic acid onto the Rh/ Al_2O_3 catalyst which had been previously dosed with 4 ml of oxygen gas as eight separate pulses. The sharp evolution of CO_2 is due to acetate decomposition on the Rh in a similar manner to that seen on single crystals (fig. 1); H_2O is tailed partly due to readsorption with the system. The high temperature desorption shoulder is due to acetate decomposition on the alumina component. Note the sharpness of the low temperature “explosion” (~ 8 K width at half height), whereas the high temperature state is a more normal width. The two spectra are offset vertically for clarity.

This decomposition then leaves C absorbed on the Rh and, as shown in fig. 4, this can be removed as CH_4 in flowing H_2 at ~ 670 K. Proof of the autocatalytic nature of the surface reaction is demonstrated in fig. 5 which is an isothermal decomposition, showing an increasing rate with increasing time during the experiment.

The high temperature tail in the desorption in fig. 3 is due to acetate species adsorbed on the support alumina. This is evidenced by their presence when no “explosive” acetate is seen (with no oxygen predose or on a Rh surface poisoned by carbon).

3. Discussion

In recent publications [8,10–12] we outlined several possibilities as sources of the autocatalytic nature of the surface decompositions. These were:

- (1) site blocking by the atomic adsorbate;
- (2) surface reconstruction;
- (3) adsorbate induced ordering.

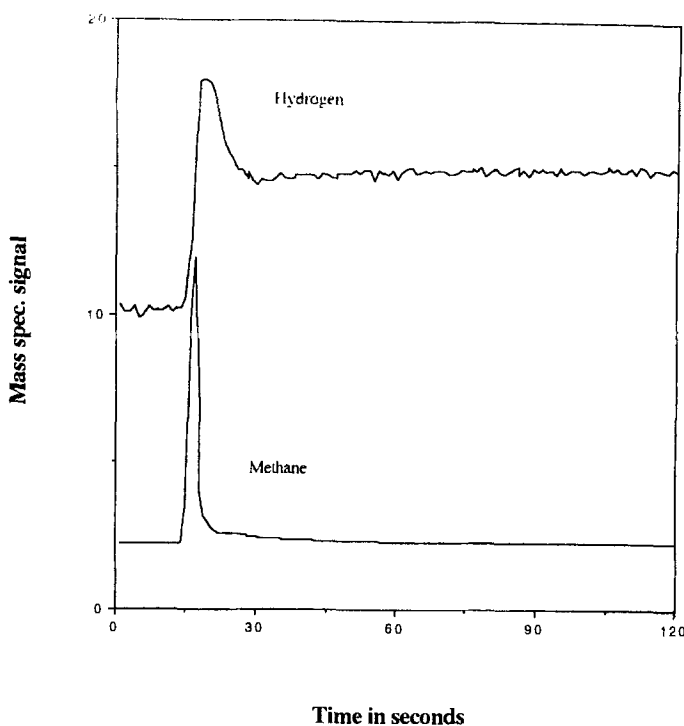


Fig. 4. Methane evolution as hydrogen is introduced over the catalyst at 670 K after an experiment of the type shown in fig. 3. The hydrogen and methane curves are offset vertically for clarity. The methane derives from C left on the Rh surface after acetate decomposition.

Point 1 was eliminated as a possibility for several reasons. Firstly, at low coverages of the acetate, but high coverages of the atomic adsorbate, no explosion is seen [11], that is, it appears that packing of the acetates themselves is implicated in the explosion. Furthermore, if on Rh(111) the O_2 is put down to exactly the correct precoverage (~ 0.25 monolayers), then approximately 0.5 monolayers of acetate adsorbed on that to remove also all the predosed O_a as water during adsorption, and then during TPD the explosion is still seen. Surface reconstruction may also be implicated, though the observation of these effects on several metals (Ni [5–7], Pd [12], and Rh [8,10,11]) and with several co adsorbates (C, N and O [11]) indicates a commonality which is due to another source. Thus proposal 3 above was favoured. Hence, in the titration experiment above the predosed O_a (which is subsequently lost) has acted as a template for ordering the acetates with respect to each other and places them in sites where they mutually block each others decomposition (fig. 6). The explosion then proceeds as outlined in the introduction above, and was mathematically described by the following equation:

$$-\frac{d\Theta}{dt} = k(1 - \Theta)^{1/2}, \quad (1)$$

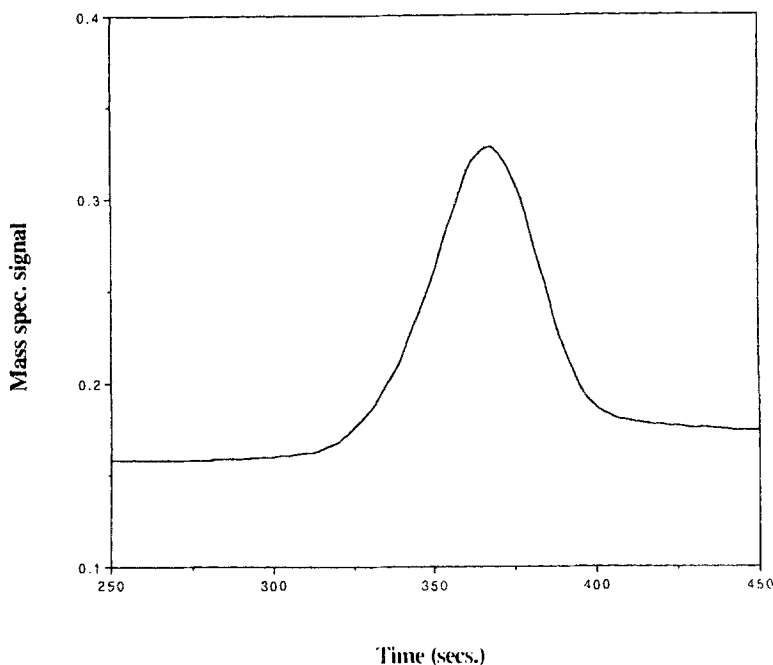


Fig. 5. Isothermal decomposition of the acetate at 500 K, showing CO_2 evolution with a rate which increases with increasing time during the experiment. Note that the time includes a heating period to reach the given temperature for the experiment and isothermal conditions were not established until around 300 s.

where k is a complex rate constant as described by Bowker and Li [8]. This mimics, in an approximate way, the kinetics of results we obtained, and the effect of increasing oxygen dose on the explosion on Rh(111) (increasing peak temperature with increasing oxygen coverage) could be explained by a decreasing number of defects within the adlayer (k in eq. (1) contains a term Θ_n , the coverage of initiation sites). Similarly the varying peak temperature for different adsorbates could be indicative of different degrees of disorder in these adlayers. However, the formulation of eq. (1) is incorrect in several ways as can be seen by inspection of fig. 1. It gives very asymmetric peaks in TPD with a sharp drop in rate as adsorbate is used up. If eq. (1) is integrated the isothermal desorption rate can be analytically derived and is given by

$$-\frac{d\Theta}{dt} = A + k^2 t/2, \quad (2)$$

where A is a constant; here the coverage term is not present since $(1 - \Theta)^{1/2}$ is directly proportional to time. This results in an isothermal desorption of the type

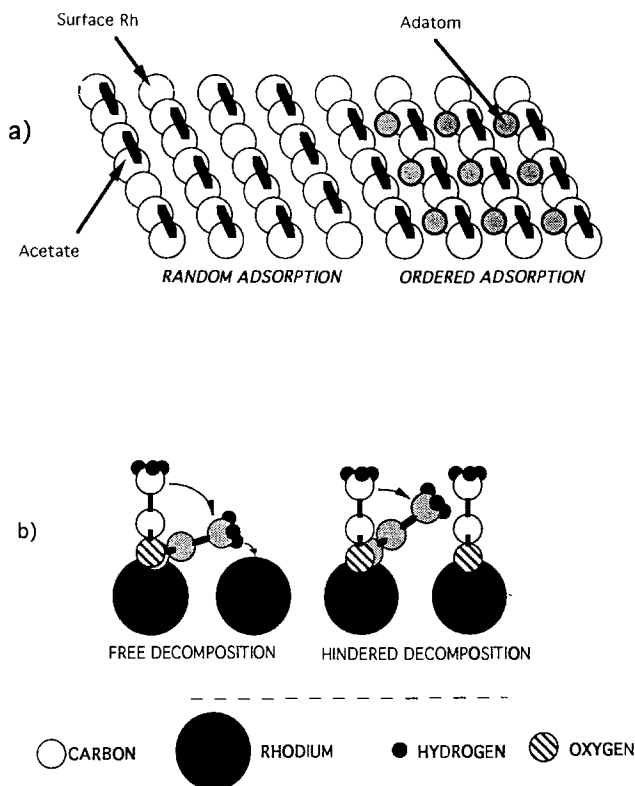


Fig. 6. Schematic models for the acetate decomposition on Rh(110) showing (a) the effect of adatoms acting as templates for ordering of the acetates, which results in self-poisoning of the decomposition reaction; (b) shows a slice through the surface in the [001] direction and indicates the mode of decomposition, that is, via methyl hydrogen abstraction by adjacent free Rh atoms. When acetates are adjacent this mechanism of decomposition is blocked.

shown in fig. 7 with a linear increase in rate with time and a sudden drop in rate again as all the adsorbate is used up. This is clearly unlike the kinds of profile observed (fig. 5, for instance) and has an unnatural shape. This treatment of the model is naive in several respects. Firstly, after 70–80% of the adsorbate has been used up (depending on the spatial distribution and geometry of *growing* islands of clean reactive surface) then the islands merge and the mathematical description changes to one with a decreasing number of active sites at the perimeter of the *shrinking* islands of adsorbate. Secondly there will be a distribution of sizes of these growing islands on the surface. However, the results with the catalyst appear to cast doubt on the island model itself, since the particles are not extensive, being on average, ~ 20 Å diameter and not capable of sustaining order over long distances. Thus it would seem that the effect would depend on a much more localised interaction. It is clearly not mediated through the gas phase since the single crystal experiments were conducted in UHV conditions. It seems that the effect may be explained in a more simple way through the formulation of classical chemical

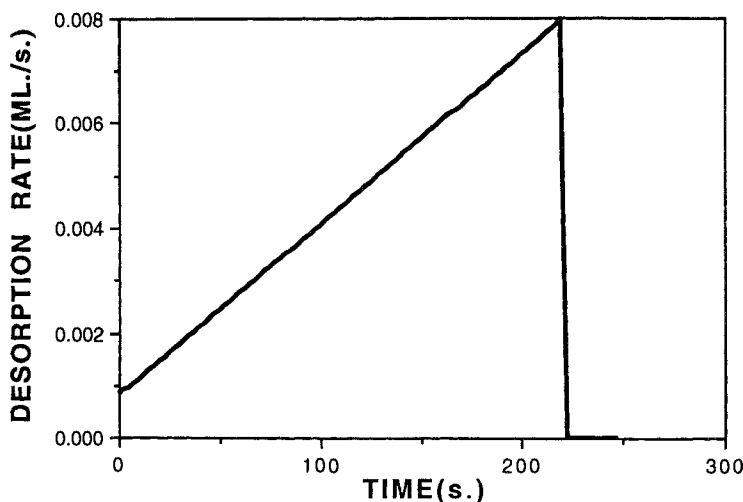
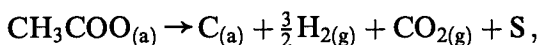


Fig. 7. An example of mathematical modelling of the isothermal desorption for the island model (eq. (2) in the text). Note the unrealistic shape of the curve. The parameters used were $A = 2.5 \times 10^{10}$ and $E = 100 \text{ kJ mol}^{-1}$ at a temperature of 400 K.

kinetics for second order autocatalytic reactions [15], where one of the products of reaction is itself necessary for the second order reaction to take place. In this particular case we can write the decomposition as



although if oxygen is present on the surface water is formed instead of hydrogen as shown above. However, the rate law is

$$-\frac{d[\text{CH}_3\text{COO}_{(a)}]}{dt} = k[\text{CH}_3\text{COO}_{(a)}][\text{S}].$$

We can rewrite this in terms of coverages of the acetate (Θ) and free sites S ($1 - \Theta$), as

$$-\frac{d\Theta}{dt} = k\Theta(1 - \Theta) \quad (3)$$

and this rate equation can be integrated to yield the time dependence of the rate as follows:

$$-\frac{d\Theta}{dt} = A'\Theta^2 \exp(kt), \quad (4)$$

where A' is a constant at fixed temperature.

The results of these considerations for curve shapes are given in fig. 8 for both isothermal and TPD experiments and show a close similarity with our experimental results, though a detailed fit has not been carried out. This description is similar

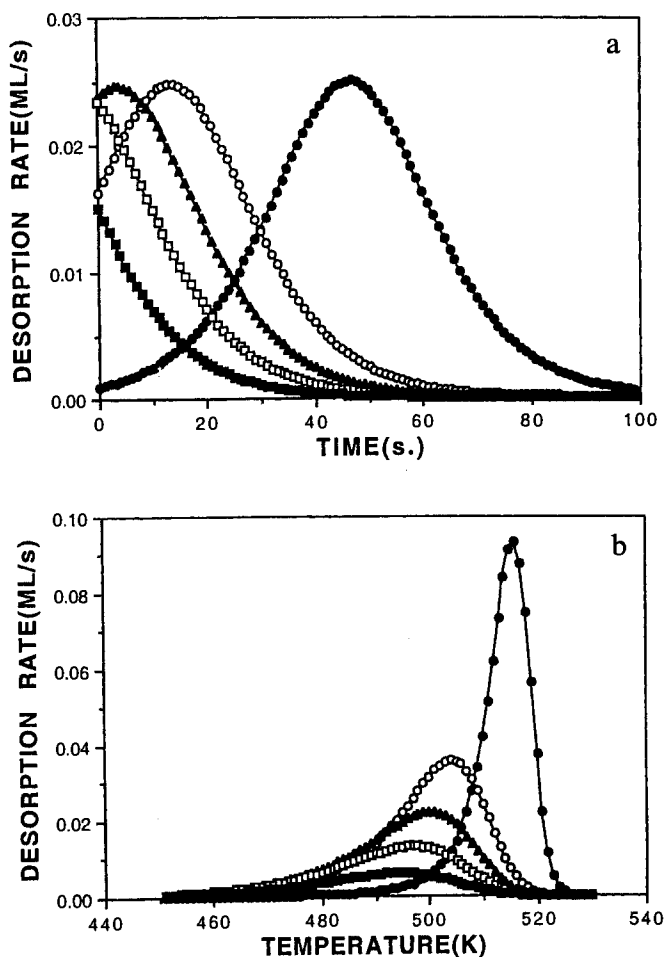


Fig. 8. (a) Mathematical modelling of the isothermal desorption at 506 K for the mobile vacancy model (eq. (4) in the text), showing a similar line shape to the experimental results. The five curves are for different initial coverages (Θ_0 in monolayers) of 0.99 (●), 0.79 (○), 0.59 (▲), 0.39 (□) and 0.19 (■). The parameters used were $A = 3 \times 10^{14}$ and $E = 150 \text{ kJ mol}^{-1}$. In the text $A' = A \exp(-E/RT) \{(1 - \Theta_0)/\Theta_0\}$. (b) Modelling of the temperature programmed desorption corresponding with the same model and parameters as in (a) (eq. (3) in the text).

to that proposed by Falconer and Madix [6], although they still propose an island model description and get poor fits to their experimental data. A full mathematical consideration of autocatalytic phenomena at surfaces is in preparation [13], and experimental work is still in progress, in particular to elucidate coverage dependent effects.

The questions then remaining are why the simple second order autocatalytic representation works and what is the role of the adatom? The overall ideas considered earlier and outlined above probably still apply, that is, the role of the adatom

is to reduce the number of vacancies in the adlayer which results in the formulation above (very little of product S, the active site, at the beginning of the decomposition) while without the adatom the number of these sites is high. From the data this clearly applies both to well defined single crystal surfaces, and to finely dispersed particles. However, with regard to the first question above, it is not at first clear why the island model does not work so well, since upon creation of the first active sites it would be envisaged that an island would grow by decomposition of acetates into the vacant sites. However this is based on a static picture of the adlayer. The success of the second order autocatalytic formalism indicates that the adlayer is homogeneous, not phase separated, which in turn implies considerable mobility of the acetate/vacancy adlayer such that the vacancies are evenly distributed over the surfaces involved.

4. Conclusions

We believe that these are significant findings and present a rather unusual demonstration of transfer of knowledge from surface science to catalysis. Furthermore the kinetics place the behaviour in the mainstream of chemical reactivity, rather than as an anomalous finding relating only to a limited number of well defined surfaces. It is proposed that they represent a general class of reactivity on surfaces and may be of significance in relation to oscillating catalytic reactions. We look forward to reports of such autocatalytic processes on other single crystal surfaces, and, following the observations reported here, to further examples of surface "explosions" being seen during desorption from catalyst surfaces.

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