

# Kinetic explosion and bistability in adsorption and reaction of acetic acid on Pd(110)

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Received 20th June 2007, Accepted 3rd September 2007

First published as an Advance Article on the web 13th September 2007

DOI: 10.1039/b709384e

The adsorption and reaction of acetic acid with Pd(110) have been studied using thermal molecular beam reaction measurements and temperature-programmed desorption. Acetic acid adsorption results in the formation of acetate species which decompose to produce coincident CO<sub>2</sub> and H<sub>2</sub> desorption from the surface. C is deposited on the surface from the dehydrogenation of the methyl group. In combination, these steps are found to exhibit unusual kinetics including (i) a “surface explosion” during heating and (ii) bistability in the reaction profile for heating and cooling curves. This is the first report of such behaviour for a complex system during *in situ* reaction.

## Introduction

The understanding of the kinetics of heterogeneous catalytic reactions (HCR) is of considerable practical importance because heterogeneous catalysis is a mainstay of the chemical industry and of environmental technologies.<sup>1</sup> HCR kinetics are also of interest due to their richness and complexity related to the interplay of adsorption and reaction steps and factors such as adsorbate–adsorbate lateral interactions, surface heterogeneity, and/or adsorbate-induced surface restructuring. These factors are manifested in such phenomena as kinetic phase transitions, oscillations, chaos, and pattern formation.<sup>2</sup> In addition, HCR are often accompanied and influenced by so-called “side” processes, including, for example, reactant diffusion into the bulk and formation of surface or subsurface oxide or carbon. In this communication, we present *in situ* kinetic data for the adsorption and reaction of acetic acid, CH<sub>3</sub>COOH, on Pd(110). This is a reaction system which illustrates such complexity in catalysis, in this case during dynamic, *in situ* reactivity measurements.

The interaction of acetic acid with the Pd surface is very relevant to the industrial synthesis of vinyl acetate monomer (VAM, CH<sub>3</sub>COOC<sub>2</sub>H<sub>3</sub>), which is carried out over catalysts containing both Pd and Au as active phases. Such catalysts appear to be alloys of these two metals, though there is some debate as to whether the rate determining step proceeds at the surface of the metals or in an aqueous phase over them (see, for instance, ref. 3 and 4). What is not in dispute, however, is that the presence of both Pd and Au is required for optimum performance of the catalysts.<sup>5</sup> It has been proposed<sup>3–7</sup> that one of the most important intermediates for this reaction is the acetate, which is produced by the dissociative adsorption of acetic acid, and it is this which is involved in coupling to ethene to produce vinyl acetate. The nature of this intermediate is of crucial importance to understanding the course of this

reaction, especially its decomposition kinetics, which has a strong influence on the selectivity of the reaction. So, this paper specifically addresses the stability of the acetate and identifies some unusual characteristics of the decomposition reaction.

## Experimental

In this work, the reactivity of the well-defined Pd(110) surface to acetic acid has been measured using a molecular beam reactor, the latter having been described in more detail elsewhere.<sup>8</sup>

It comprises a stainless steel UHV chamber maintaining a base pressure of  $\sim 2 \times 10^{-10}$  mbar (95% H<sub>2</sub>) which increased to  $\sim 6 \times 10^{-10}$  mbar during the course of some of the adsorption experiments. It consists of the molecular beam itself, which delivers a circular beam at the sample of 2.9 mm diameter with a flux of  $1.5 \times 10^{17}$  molecules m<sup>-2</sup> s<sup>-1</sup>, or about 0.015 monolayers of molecules s<sup>-1</sup> with respect to the number of surface atoms. The Pd(110) crystal was mounted on a custom-built holder in the chamber centre. In the same horizontal plane is the molecular beam enclosure, a rear-view retarding field analyser system with a coaxial electron gun (supplied by VG Microtech) for low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), and a set of differentially pumped chambers which comprise an angle resolved mass spectrometer. Also in the main UHV chamber is a quadrupole mass spectrometer (QMS) (Hiden Analytical Limited) employed for residual gas analysis (RGA). The QMS provides an indication of the angle-integrated partial pressure within the vacuum chamber, since no direct line of sight exists between the sample and detector.

The Pd(110) crystal (5N purity, Metal Crystals and Oxides Ltd), cut and polished in the (110) plane, could be heated and cooled in the chamber to between 110 and 1040 K. The sample was heated by direct contact with two tungsten wires, which passed through grooves in the edge of the crystal and were resistance heated. The heating rate was set at 1 K s<sup>-1</sup> in the temperature range of interest. Sample cooling was performed

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by close proximity of the sample mount to a liquid N<sub>2</sub> reservoir, connected by a Cu braid and a sapphire thermal switch. The temperature was recorded through a chromel–alumel thermocouple attached to the sample by a small hole drilled in the edge parallel with the surface plane. The surface was cleaned by cycles of Ar<sup>+</sup> bombardment (500 eV, 6 mA cm<sup>−2</sup>, 30 min), annealing (850 K, 20 min) and flashing (1020 K, 2 min). Between successive exposures to acetaldehyde, the Pd(110) surface was heated in O<sub>2</sub> to remove C from the surface.

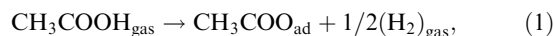
## Results and discussion

Earlier, we have shown that acetate species are readily formed on Pd(110), and that the acetate-decomposition products, CO<sub>2</sub> and hydrogen, exhibit unusual desorption characteristics.<sup>7,9</sup> In particular, they manifest the “surface explosion” phenomenon,<sup>10</sup> a kinetic process interpreted as a second-order, homogeneous autocatalytic decomposition.<sup>11–13</sup> This leads to anomalously small half-widths for temperature-programmed desorption peaks which can be as small as 6 K for this system<sup>7,9</sup> and 5 K in some other cases.<sup>14,15</sup>

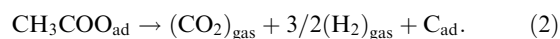
In the present case, we have used the molecular beam reactor, which is normally employed in an isothermal reaction mode,<sup>8</sup> to examine the anaerobic reaction of acetic acid on Pd(110) in a temperature-programmed mode with the reactant continuously present in the gas phase. The results of such an experiment are shown in Fig. 1. The only significant products from the surface are CO<sub>2</sub> and hydrogen, and it can be seen in Fig. 1 that these show generally the same profile upon heating or cooling, but there are some detailed differences. To scrutinise the reaction kinetics, the experiment can be broken down into several stages.

In stage 1, the surface begins in a clean state and acetic acid is introduced to the surface at 340 K by opening a beam-

blocking flag. The acetic acid then adsorbs and only hydrogen evolves from the surface. This is due to acetate formation occurring *via* the following surface reaction



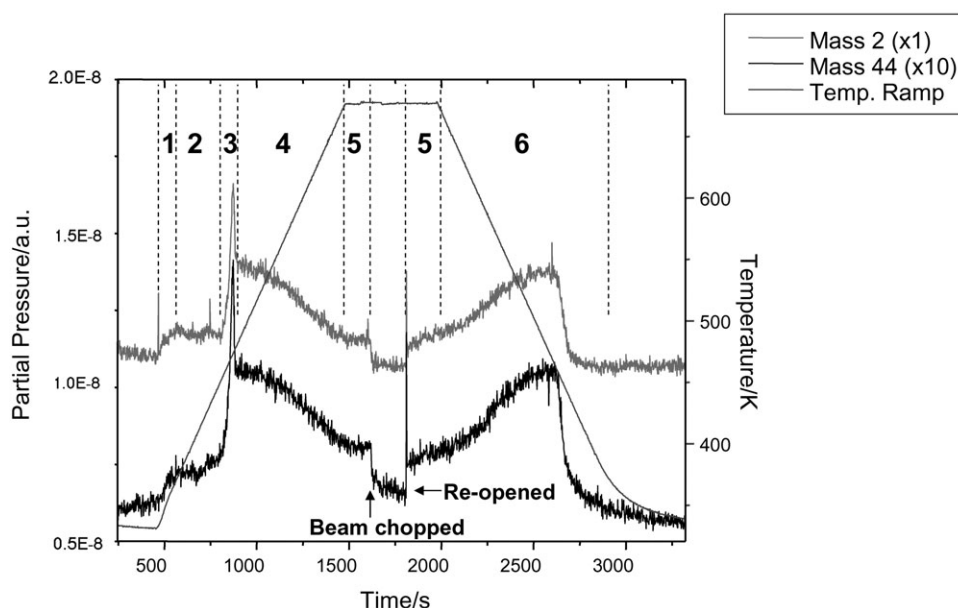
where the subscripts “gas” and “ad” correspond to gas-phase and adsorbed species, respectively. The adsorbed acetate begins to decompose almost immediately upon heating. The desorption spectrum in Fig. 2a shows that, on the clean surface, the acetate starts to break down at  $\approx 330$  K (giving coincident CO<sub>2</sub> and H<sub>2</sub> evolution). Thus, both CO<sub>2</sub> and H<sub>2</sub> are seen in stage 2 of Fig. 1, due to acetate decomposition resulting also in the formation of surface carbon,



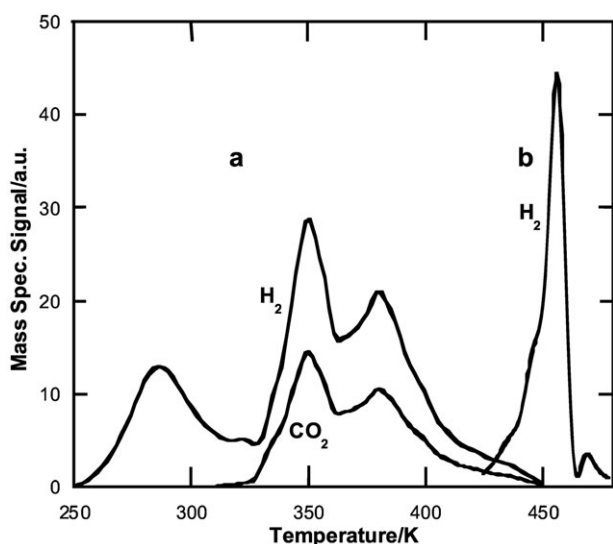
At stage 3, there is a “light-off” of CO<sub>2</sub> and H<sub>2</sub> production with a very sharp maximum. This occurs at the same temperature as the surface explosion shown in Fig. 2, which occurs when a layer of carbon has been deposited on the surface first.<sup>7,9</sup> In the case of Fig. 1, the light-off peak is approximately 7 K in width. This “light-off” is the autocatalytic acetate decomposition and is a non-steady state phenomenon.

Stage 4 follows and is due to true decomposition of gas phase acetic acid on the Pd(110) surface, but obviously it occurs on a surface on which carbon has already been deposited in step (2). The rate declines as temperature increases because the coverage of acetate diminishes on the surface, since this is now above its decomposition temperature. However, there is still a real rate of decomposition even at 770 K.

Stage 5 is an isothermal part of the experiment, and the rate is near constant between 1500 and 1650 s. At that point, the beam was interrupted for 200 s, to check the background signals from the chamber, which indeed returned to



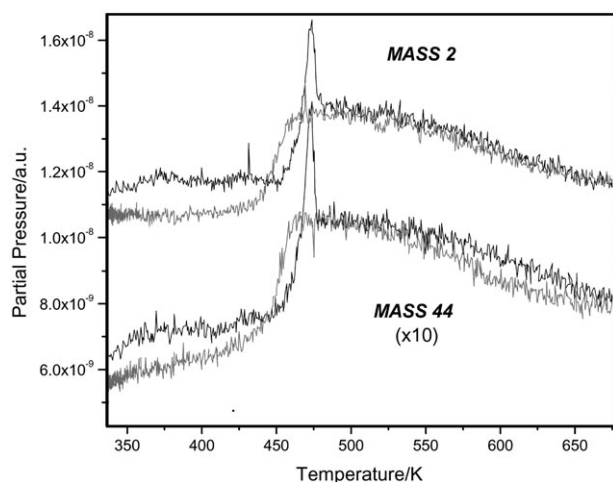
**Fig. 1** Temperature-programmed reaction of acetic acid on Pd(110), showing the gas-phase products and temperature profile during heating and cooling. The labelled stages of the experiment are described in detail in the text.



**Fig. 2** Temperature-programmed desorption spectra after the adsorption of acetic acid on Pd(110). Curves (a) show the hydrogen and carbon dioxide evolution during heating after the adsorption of 2 L of acetic acid at 220 K, whereas curve (b) is after deposition of about 0.5 monolayers of C on the surface first, followed by 2 L of acetic acid at 323 K (the CO<sub>2</sub> desorption curve is identical).

their original level that existed before the molecular beam experiment.

Upon re-opening the beam the rate attains essentially the same steady-state level and in stage 6 the sample is cooled in a linear fashion for most of the period. The shape is the same as that for the heating sequence, except for the absence of the 'surface explosion' peak. This is confirmed in Fig. 3, which shows the two curves superimposed on a temperature axis. It is clear that there is no significant difference, within experimental uncertainty, in reaction rate between 500 and 670 K, whether heating or cooling. However, there are several differences at the lower temperature end of the reaction profile. Firstly, the explosive peak is missing from the cooling curve; this is unsurprising since it is not a peak from direct reaction with



**Fig. 3** Data of Fig. 1, shown as a function of temperature, with the heating (black curve) and cooling (grey curve) curves superimposed, demonstrating the hysteresis in the reaction.

the gas, but it is a surface acetate decomposition peak occurring at high acetate coverage, and in the cooling experiment the acetate is not at high coverage. In addition, there is some hysteresis in the curves with overshoot of the rate on the cooling curve to lower temperatures before it drops again to low rate. The rate drops because of surface poisoning by acetate species and low decomposition rate of the acetate. On the heating curve the rate appears higher up to 450 K because of the beginning of acetate decomposition on the otherwise clean surface (that is, little surface carbon is present at this stage and the acetate and carbon coverages are increasing on the surface).

One thing about these data is very surprising, that is, during the acetate decomposition throughout this long experiment, carbon is being deposited onto the surface, at least above  $\approx 350$  K. However, this appears to have little effect on the reaction and appears not to poison it significantly. Thus, if the decline in rate on the up curve was due to such poisoning, we would not expect the rate to increase again on cooling. The reason there is so little effect on acetic acid decomposition is that the carbon produced in the reaction is lost to the bulk of the crystal, as described elsewhere,<sup>7,16</sup> and there is no evidence of the high levels of C deposited being present on the surface. C begins to diffuse into the subsurface of the crystal at about 430 K, and proceeds at a high rate above 500 K. The amount of carbon deposited in the whole experiment is  $\approx 20$  monolayers. If present on the surface, it would be dominant in Auger spectra, whereas it is hardly evident. The poisoning of the reaction on the cooling curve below 440 K is due to the build-up of both acetate and carbon.

It is of interest to discuss the possible origins of the bistability in the reaction kinetics (Fig. 3) at temperatures below 450 K. In general, this phenomenon may be either (i) apparent, that is, it results from steps which are slow on the time scale of measurements, or (ii) true due to either (a) non-linear reaction steps or (b) a first-order phase transition in the adsorbed overlayer.

Although at present, we are not able to unequivocally distinguish between these alternatives, there are some arguments against reasons (ii). Purely chemical bistability [item (iia)] results from the interplay of a few non-linear steps. A classical example is CO oxidation on Pt-group metals, for instance, on Pt(111),<sup>17</sup> Pt(110),<sup>18</sup> supported Pt,<sup>19</sup> and Ir(111).<sup>20</sup> In this and other real catalytic reactions, at least one of the steps always has a high activation energy. Accordingly, one or both of the two reaction rates, corresponding to two bistable regimes, show a significant dependence on temperature or, more specifically, depend on temperature in different ways.<sup>21</sup> This means that the ratio of the rates is expected to vary strongly with temperature as well. In CO oxidation, for example, this dependence is related to the dependence of CO desorption rate on temperature.<sup>21,22</sup> In the reaction under consideration, in contrast, the temperature variations of the reaction rates on the up and down branches in the bistability region (below the explosion) are relatively weak and are nearly identical above 500 K.

Cyclic TPD measurements (Fig. 2 in ref. 7) indicate that the acetic acid decomposition products result in appreciable suppression of the acetate decomposition. The most probable

reason for this finding is attractive lateral adsorbate–adsorbate interaction stabilizing acetic acid adsorption. This interaction may easily result in a first-order phase transition in the adsorbed overlayer [item (iib)]. The bistability related to such a phase transition is also expected to be strongly dependent on temperature. In the experiment, as already noted above, this is however not the case.

Slow steps [item (i)] are more probable. Here, one can distinguish between purely kinetic steps (for instance, slow reaction steps and/or slow diffusion of carbon into the substrate) or steps related with adsorbate-induced changes in the surface. In the system under consideration, both these scenarios are possible. For example, the adsorbate may induce the formation of the  $(1 \times 2)$  missing-row structure. On the clean surface, the transition back to the  $(1 \times 1)$  phase typically occurs at temperatures above 370 K<sup>23</sup> and the  $(1 \times 2)$  phase is metastable below that temperature. In our case, in the presence of adsorbates, surface restructuring to, or from, the metastable phase may occur at higher temperatures and accordingly may be one of the reasons for the observed bistability.

We may ask ourselves what relevance this has to the industrial synthesis of vinyl acetate. It is likely that the acetate intermediate will dominate the surface, since it is the most stable intermediate. It might be imagined that the explosive decomposition of acetate seen above is restricted only to single crystals, but this is incorrect. We have shown earlier that such unusual kinetics are seen both on Rh single crystals, and on supported Rh catalysts.<sup>12,13</sup> The temperature range of the decomposition on Pd is also similar to that of the industrial reaction. That nature of the decomposition of acetate implies some danger for industrial catalytic VAM synthesis. If conditions are such that acetate builds up to a high level, then non-steady state decomposition may occur, which could lead to rapid pressure excursions. However, the loading of metal is usually fairly low, which may therefore limit this problem.

Returning to the fact that Au is added to the catalyst to give improved performance, it may well be that one role of this is to reduce the carbon formation described above, as we<sup>16,25</sup> and others,<sup>26</sup> have proposed recently.

Finally, it is appropriate to note that according to the conventional terminology used in heterogeneous catalysis, carbon formation on the surface and subsurface layers often represents “complicating” or “side” processes. Although the importance of such steps has long been recognized, the understanding of the corresponding kinetics is limited. In applied studies, the kinetics are often too complex to clearly distinguish such “side” processes. In academic studies, researchers tend to avoid the regimes complicated by such parallel processes. In combination with our earlier work,<sup>7,9</sup> the present study indicates that such processes may result in fairly unusual kinetic phenomena. Among other recent interesting examples of such parallel processes, we may mention oxide formation during CO oxidation on supported Pd<sup>22</sup> and reports of alloy formation in the Cu/ZnO catalyst for methanol synthesis.<sup>24</sup>

## Conclusion

In summary, our present study identifies a number of unusual and interesting features of the kinetics of acetic acid decom-

position occurring under pseudo steady-state conditions. In particular, the acetate intermediate shows the characteristics of a “surface explosion” at high coverage, and this is induced by the presence of carbon on the surface of the crystal. This has the effect of stabilizing, and ordering the acetate and this, in turn, induces some bistability into the kinetics of the process. It is of interest that on the reverse branch of the kinetics (decreasing temperature), the influence of carbon is not so manifest, due to subsurface diffusion of carbon. All of these findings have implications for catalytic processes in which acetic acid is used as the reactant, such as vinyl acetate synthesis.

## Acknowledgements

We are grateful to EPSRC and to BP Chemicals for support for C.M. under the Industrial Case award scheme.

## References

- 1 J. M. Thomas and W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis*, VCH, Weinheim, 1997.
- 2 (a) F. Schüth, B. E. Henry and L. D. Schmidt, *Adv. Catal.*, 1993, **39**, 51–127; (b) G. Ertl, *Adv. Catal.*, 2000, **45**, 1–69; (c) V. P. Zhdanov, *Surf. Sci. Rep.*, 2002, **45**, 233–326.
- 3 S. Nakamura and T. Yasui, *J. Catal.*, 1971, **23**, 315–320.
- 4 B. Samanos, P. Boutry and R. Montarnal, *J. Catal.*, 1971, **23**, 19–25.
- 5 (a) W. Provine, P. Mills and J. Lerou, *Stud. Surf. Sci. Catal.*, 1996, **101**, 191–201; (b) N. Macleod, J. Keel and R. M. Lambert, *Appl. Catal., A*, 2004, **261**, 37–46.
- 6 D. Stacchiola, F. Calaza, L. Burkholder and W. T. Tysoe, *J. Am. Chem. Soc.*, 2004, **126**, 15384–15385.
- 7 M. Bowker, C. Morgan and J. Couves, *Surf. Sci.*, 2004, **555**, 145–156.
- 8 M. Bowker, *Appl. Catal.*, 1997, **160**, 89–96.
- 9 N. Aas and M. Bowker, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 1249–1256.
- 10 J. McCarty, J. Falconer and R. J. Madix, *J. Catal.*, 1973, **30**, 235–246.
- 11 A. Frost and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 2nd edn, 1961, p. 19.
- 12 T. Cassidy, M. Allen, Y. Li and M. Bowker, *Catal. Lett.*, 1993, **21**, 321–327.
- 13 M. Bowker, T. Cassidy, M. Allen and Y. Li, *Surf. Sci.*, 1994, **307–9**, 143–149.
- 14 J. Falconer and R. J. Madix, *Surf. Sci.*, 1974, **46**, 473–479.
- 15 M. Bowker and Y. Li, *Catal. Lett.*, 1991, **10**, 249–255.
- 16 M. Bowker, C. Morgan, N. Perkins, R. Holroyd, E. Fourre, F. Grillo and A. MacDowall, *J. Phys. Chem. B*, 2005, **109**, 2377–2386.
- 17 M. Berdau, G. G. Yelenin, A. Karpowicz, M. Ehsasi, K. Christmann and J. H. Block, *J. Chem. Phys.*, 1999, **110**, 11551–11573.
- 18 B. L. M. Hendriksen and J. W. M. Frenken, *Phys. Rev. Lett.*, 2002, **89**, 046101.
- 19 V. Johaneek, M. Laurin, A. W. Grant, B. Kasemo, C. R. Henry and J. Libuda, *Science*, 2004, **304**, 1639–1644.
- 20 S. Wehner, F. Baumann and J. Kuppers, *Chem. Phys. Lett.*, 2003, **370**, 126–131.
- 21 V. P. Zhdanov and B. Kasemo, *Surf. Sci. Rep.*, 1994, **20**, 111–189.
- 22 T. Schalow, B. Brandt, M. Laurin, S. Schauermaann, J. Libuda and H. J. Freund, *J. Catal.*, 2006, **242**, 58–70.
- 23 V. R. Dhanak, G. Comelli, G. Paolucci, K. C. Prince and R. Rosei, *Surf. Sci.*, 1992, **260**, L245–251.
- 24 J. Nakamura, Y. Choi and T. Fujitani, *Top. Catal.*, 2003, **22**, 277–285.
- 25 M. Bowker and C. Morgan, *Catal. Lett.*, 2004, **98**, 67–67.
- 26 Y. F. Han YF, D. Kumar, C. Sivadinarayana, A. Clearfield and D. W. Goodman, *Catal. Lett.*, 2004, **94**, 131–134.