Catalysis Letters 34 (1995) 313–320

Oscillations of CO and CO + H_2 oxidation in air over supported and unsupported Pt catalysts

Y.Q. Deng, T.G. Nevell[1]
Division of Chemistry, University of Portsmouth, Portsmouth, PO1 2DT, UK

and

M.G. Jones
City Technology Ltd, Walton Road, Portsmouth, PO6 1SZ, UK

Received 8 November 1994; accepted 16 June 1995

Oscillation behaviour of the oxidation of CO (0.2–2.2%) in air over Pt wire coils and over Pt/Al_2O_3 catalysts deposited onto the coils (pellistors) has been investigated. The waveforms differ considerably between the two catalytic systems. Over unsupported Pt at 240–260°C, regular oscillations were accompanied by slowly declining activity and by deposition of carbon. Over supported Pt at 110–180°C, relatively complex but sustained oscillation occurred by a different mechanism. This oscillation was greatly enhanced by H_2 (0.25–1.0%), and may involve fluctuations in the concentrations of CO and H_2 around the supported catalyst.

Keywords: oscillation; CO + H_2 cooxidation; chemical sensor; pellistor; platinum; platinum/alumina

1. Introduction

Previous studies [1–14] of the oscillation of CO oxidation on platinum and palladium have used catalysts in various forms (M/Al_2O_3 or M/SiO_2, mesh, film, foil, ribbon and wire). Observations have involved monitoring the surface state or temperature of the catalyst and the composition of products. Oscillations over supported and unsupported catalysts are not readily compared, however, because of widely differing experimental conditions. It is unclear whether the absence of fine structure of some observed waveforms is due to the synchronisation of contributing oscillatory processes in relatively large packed beds, or to the insufficiently rapid or sensitive response of some methods of observation [15]. Oscillations in catalytic

---

[1] To whom correspondence should be addressed.

systems have been reviewed [15,16]. Well-established explanations of oscillatory behaviour include alternating oxidation and reduction of the surface [17,18], the formation and autocatalytic oxidation of carbon [19,20], and reconstruction of surface structure [21,22]. Luss, Schmidt and their colleagues have reported spatial heterogeneity and the phenomenon of synchronisation during oscillations in catalytic systems [23–25]. Suggestions have also been made of possible contributions by heterogeneous–homogeneous processes or by "impurities" in the feed gas [26–28].

A platinum coil, as used for the detection of flammable gases [29], is a suitable tool to investigate oscillation behaviour in catalytic combustion [28]. Uncoated, the coil acts as heater, temperature indicator and unsupported catalyst. When supported catalysts, such as Pt/Al_2O_3, are deposited onto the coil, they act as heater and temperature indicator only. This system not only allows a very high sensitivity (temperature resolution of 0.01 K) but also has a rapid response time and a very small "thermal lag". In this study, oscillations in CO oxidation over both supported and unsupported Pt have been observed under similar reaction conditions, and interactions between the catalytic oxidations of CO and H_2 have also been investigated. Observations of oscillations in mixtures of $CO + H_2$ in air over supported catalysts may have a potential application for the selective detection of these gases using a catalytic flammable gas sensor.

2. Experimental

Coils (6 turns, 1.5 mm length, 1 mm diameter) of Pt wire (0.025 mm diameter, Johnson Matthey, 99.97%) each spot-welded to a transistor header, were used as unsupported Pt catalysts. The supported catalysts were prepared by impregnation of γ-Al_2O_3 (Johnson Matthey, 99.99%) with aqueous $(NH_4)_2PtCl_4$ (Johnson Matthey). The amounts of γ-Al_2O_3 and the solution were adjusted to prepare catalysts containing 15 mass% of Pt metal. The resulting slurry was deposited dropwise onto similar coils of Pt wire, forming "pellistors" [30]. The precursors were dried at room temperature, then calcined in air (550°C, 5 h). Some physicochemical properties of the catalysts have been reported previously [31]; in particular, the degree of dispersion was low.

Mixtures in air (filtered by active carbon and silica gel) of CO (BOC Tech. grade) 0.2–2.2% and H_2 (BOC CP grade) 0.25–1.0% were prepared in a cylindrical vessel (550 cm^3), using a vacuum system (10^{-4} kPa). Gas mixtures were filtered again before being introduced into the reaction system.

A conventional flow reaction system (20 $cm^3\ min^{-1}$ at atmospheric pressure) was used for kinetic measurements. The borosilicate glass reactor consisted of a U-tube with two side-arms for the passage of gas mixtures. A catalytic pellistor and a non-catalytic compensating pellistor were mounted centrally in the ends of tube with the compensator upstream, so that flammable gas reached the sensing element by diffusion. The temperatures of the pellistors, determined from prior calibration, were controlled and monitored using a Wheatstone bridge network [32]. Reaction rate was proportional to the out-of-balance voltage, V, across the network.

3. Results

3.1. CO OXIDATION OVER UNSUPPORTED Pt AND Pt/Al_2O_3 CATALYSTS

A typical response, V, of CO oxidation in air as a function of reaction temperature is shown in fig. 1 (curve 1). When both supported and unsupported Pt catalysts were exposed to CO/air at low temperature, a short response (ca. 4–6 s) was followed by loss of signal, apparently caused by the self-inhibition of CO oxidation [18]. However, above a critical temperature (ca. 110°C for Pt/Al_2O_3 and ca. 240°C for unsupported Pt) the response was maintained, and a superimposed periodic oscillation was also observed. The critical temperature was raised by increasing the concentration of CO. For 0.75% CO in air, these oscillations occurred at 240–260°C over unsupported Pt and at 110–180°C over Pt/Al_2O_3. In these ranges of temperature, the regime of the reaction was changing between chemical control (V increasing rapidly with rising temperature) and mass-transport control (V decreasing slowly) [30,33].

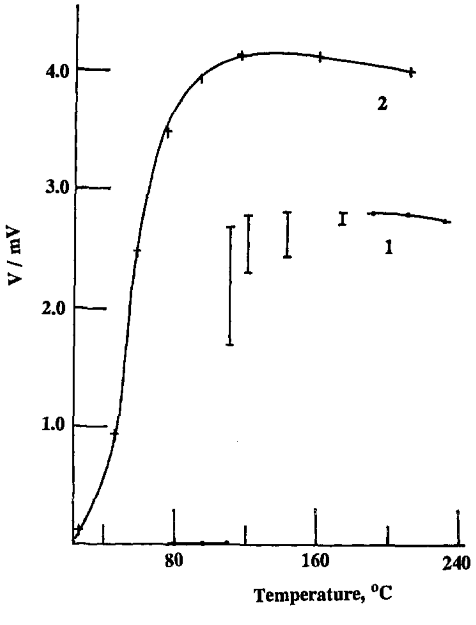

Fig. 1. Responses of a Pt/γ-Al_2O_3 pellistor to CO and H_2 oxidation in air as a function of temperature: (1) CO (0.75% v/v)/air, (2) H_2 (0.5% v/v)/air.

For the unsupported Pt catalysts, an oscillation involving alternate suppression and enhancement of the response was triggered during the course of each experiment in the range 240–260°C (fig. 2). Thus, when a mixture of CO in air was introduced, the response passed through a maximum and then oscillation commenced suddenly after ca. 45 s. At later stages fine structure was revealed, i.e. there were some minor high-frequency oscillations during each major cycle. Activity declined progressively, the frequency and amplitude of the major cycles fluctuated, and after ca. 20 min the surface of the Pt catalyst had become wine-red. Electron microscopy showed islands (ca. 20 μm) of flaky deposits on the surface of the coil. The deposits were readily burned off in air at higher temperature and therefore were probably carbon. It is observed that the brightness of the surface was decreased after the coil was subjected to several reaction–combustion sequences, indicating considerable reconstruction of the surface. Above 260°C there was no decline in activity, no evidence for deposition of carbon, and no oscillation.

With supported Pt, sustained oscillation behaviour was produced simultaneously with the initial response to CO/air mixtures (fig. 3). Activity remained constant and no evidence of carbon deposition could be found. The waveforms were much more complex with a multipeak structure, but were relatively stable in frequency and amplitude. Generally, the amplitude of oscillation over supported

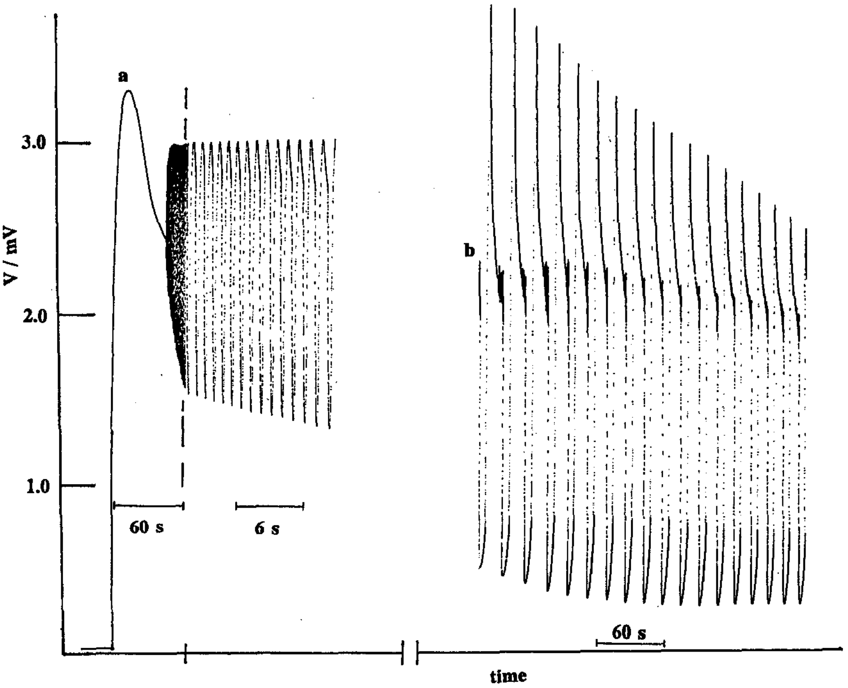

Fig. 2. Typical oscillation of CO (0.75% v/v)/air oxidation over unsupported Pt at 240°C: (a) over 0–80 s, (b) >100 s.

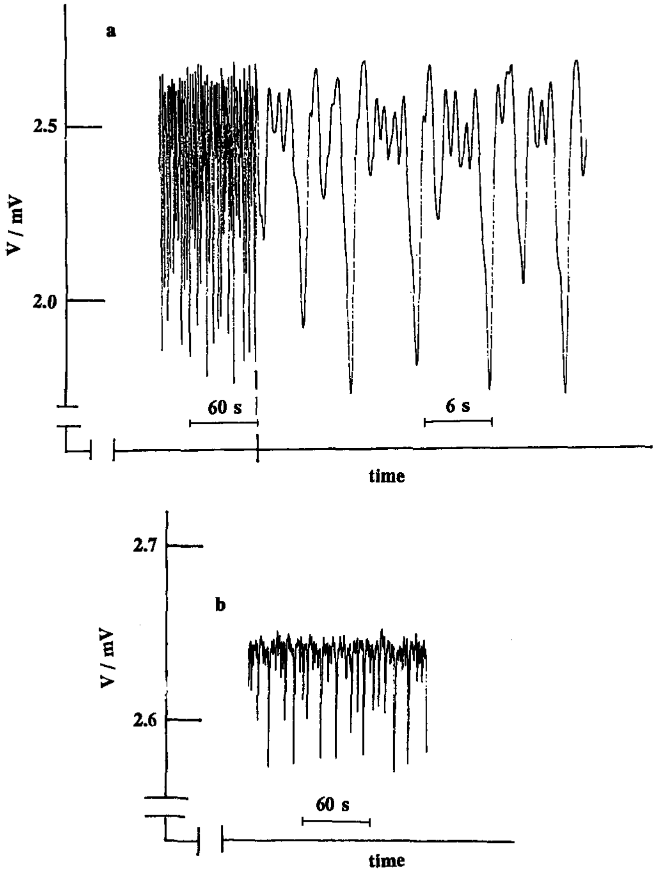

Fig. 3. Typical oscillation of CO (0.75% v/v)/air oxidation over Pt/γ-Al_2O_3: (a) 110°C, (b) 175°C.

Pt was lower than that over the unsupported metal. Frequencies were respectively 10–15 min^{-1} and 5–80 min^{-1} for supported and unsupported Pt.

3.2. INFLUENCE OF H_2 ON THE OSCILLATION OF CO OXIDATION

Because of the variations in the activity of unsupported Pt (coils) during oscillations, oxidation of mixtures of H_2 + CO in air was carried out only over supported Pt catalysts. These were reactive to H_2 in air at temperatures above ca. 40°C (fig. 1, curve 2). Responses to H_2 were much greater than to CO, due mainly to the higher diffusivity of H_2. The dependence of activity on temperature showed a progressive change from chemical control to mass-transport control over the temperature range 80–120°C. No oscillation could be found within the range of H_2 concentrations 0.2–1.0% at temperatures 40–240°C.

With H_2 + CO/air mixtures, minimum temperatures for an observable reaction were between those for the separate catalytic reactions. The features of the dependence of catalytic activity on temperature were very similar to those for CO oxidation. Oscillation behaviour was also produced by these mixtures at temperatures in the transition range between chemical control and mass-transport control. The presence of H_2 considerably affected the waveforms (fig. 4). In low concentrations, H_2 increased their complexity but had little effect on amplitude. However, with a concentration of H_2 of 1% the waveforms became more regular with higher frequency. As the concentration of CO was increased the direction of oscillation was first reversed (not shown) and then became centred, i.e. the oscillation changed from periodic "inhibition" to periodic "promotion", and then to alternating "inhibition" and "promotion". In addition, the amplitude of CO (2.2%) + H_2 (1.05%) oscillations was greatly enhanced, by as much as a factor of 7 compared with oscillations in the absence of H_2.

4. Discussion

The different oscillation behaviour that occurred over unsupported and sup-

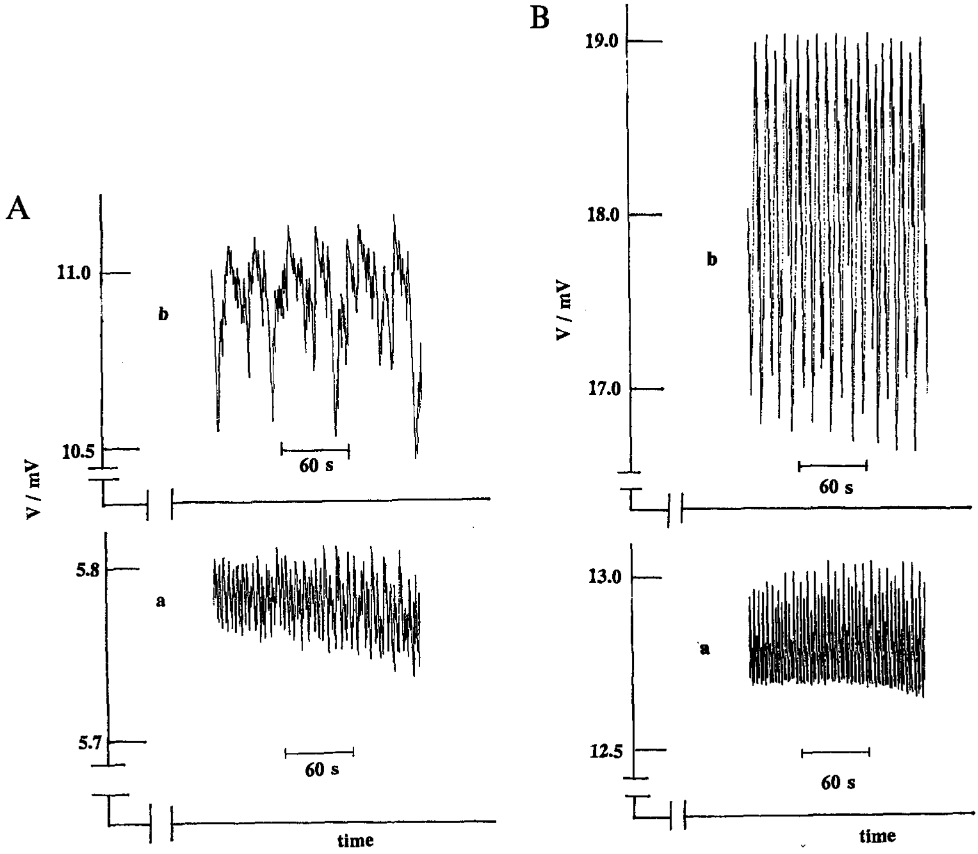

Fig. 4. Oscillation of $(CO+H_2)$/air mixtures over Pt/γ-Al_2O_3 at 175°C: (A) H_2 0.25%, CO (a) 0.75%, (b) 2.2%; (B) H_2 1.0%, CO (a) 0.75%, (b) 2.2%.

ported Pt was probably related to different oscillation mechanisms. Although it has been suggested [34,35] that impurities, either in the catalyst or from compressed gases, may cause oscillation, it is now accepted that the oscillations are associated with the transformations at the crystallite level and occur in the absence of impurities [15,18]. For Pt wire, the catalytic surface was relatively uniform and therefore the waveforms were more regular. Since oscillation was only triggered after an induction period during which response was reduced by deposition of carbon, the oscillation may have been driven by surface carbon species, whose formation would be associated with competition between oxidation and disproportionation of strongly adsorbed CO. As suggested previously [19,20], accumulation of such species would cause progressive decline in activity, while alternating adsorption and oxidation would give rise to oscillations. Since oscillations were observed only over a narrow temperature range, the adsorbed precursor of surface carbon species is relatively unstable. The fine structure observed during each major cycle may be due to spatial variations of the oscillation on the catalyst surface.

With the more active supported Pt, the chaotic waveforms would be caused by the lack of uniformity of surface of the catalyst. Since there was no induction period, no progressive decline in activity and no other evidence for carbon deposition, the mechanism will have been different. Oscillations occurred at temperatures in the transition range from chemical control to mass-transport control, so that pore diffusion of reactive species may have been involved.

It is well-known that CO oxidation over Pd and Pt catalysts is promoted by H_2 and H_2 oxidation is inhibited by CO [36,37]. Our observed intermediate temperatures for the onset of reaction in mixtures of $CO + H_2$ in air are consistent with this. There is also a striking similarity between the oscillation reported here and those previously observed for the non-catalytic oxidations of H_2 and $CO + H_2$ [16]. Hence, over the supported catalysts and particularly with richer mixtures, a heterogeneous–homogeneous reaction [26] may have occurred resulting in more regular waveforms and enhanced amplitudes.

Acknowledgement

YQD was supported by a Royal Society China Fellowship.

References

[1] J. Rathousky and V. Hlavacek, J. Catal. 75 (1982) 122.
[2] D.T. Lynch and S.E. Wanke, J. Catal. 88 (1984) 333.
[3] H. Okamoto, G. Kawamura and T. Kudo, J. Catal. 87 (1984) 1.
[4] D.J. Kaul and E.E. Wolf, J. Catal. 93 (1985) 321.
[5] R. Imbihl, M.P. Cox and G. Ertl, J. Chem. Phys. 84 (1986) 3519.

[6] L.F. Razon and R.A. Schmitz, Catal. Rev. Sci. Eng. 28 (1986) 89.
[7] R. Sant and E.E. Wolf, J. Catal. 110 (1988) 249.
[8] P.K. Tsai, M.B. Maple and R.K. Herz, J. Catal. 113 (1988) 453.
[9] J. Kapicka and M. Marke, J. Catal. 119 (1989) 508.
[10] J.C. Kellow and E.E. Wolf, Chem. Eng. Sci. 45 (1990) 2597.
[11] H.H. Rotermund, W. Engel, M. Kordesch and G. Ertl, Nature 343 (1990) 355.
[12] P.K. Tsai, M.G. Wu and M.B. Maple, J. Catal. 127 (1991) 512.
[13] M. Ehsasi, M. Berdau, A. Karpowicz, K. Christmann and J.H. Block, in: *Proc. 10th Int. Congr. on Catalysis*, Budapest, 19–24 July 1992, eds. L. Guczi, F. Solymosi and P. Tétényi (Akadémiai Kiadó, Budapest, 1993) p. 321.
[14] K.K. Tenchev, L.A. Petrov, G.A. Savelieva and A.S. Sass, Appl. Catal. 83 (1992) 31.
[15] F. Schüth, B.E. Henry and L.D. Schmidt, Adv. Catal. 39 (1993) 51.
[16] S.K. Scott, *Chemical Chaos* (Clarendon Press, Oxford, 1991) chs. 9, 10.
[17] J.E. Turner and M.B. Maple, Surf. Sci. 147 (1984) 647.
[18] N. Hartmann, R. Imbihl and W. Vogel, Catal. Lett. 28 (1994) 373.
[19] V.A. Burrows, S. Sundaresan, Y.J. Chabal and S.B. Chrismann, Surf. Sci. 180 (1987) 110.
[20] N.A. Collins, S. Sundaresan, Y.J. Chabal and S.B. Christnann, Surf. Sci. 180 (1987) 136.
[21] F. Schüth and E. Wicke, Ber. Bunsenges. Phys. Chem. 93 (1989) 191.
[22] S.B. Schwartz and L.D. Schmidt, Surf. Sci. 206 (1988) 169.
[23] L. Lobban and D. Luss, J. Phys. Chem. 93 (1989) 6530.
[24] L. Lobban, G. Philippan and D. Luss, J. Phys. Chem. 93 (1989) 773.
[25] S.B. Schwartz and L.D. Schmidt, Surf. Sci. 206 (1988) 169.
[26] M. Sheintuch and D. Luss, J. Catal. 68 (1981) 245.
[27] P. Varghese, J.J. Carberry and E.E. Wolf, J. Catal. 55 (1978) 76.
[28] T. Lamb, R.P. Scott, P. Watts, B. Holland, S.J. Gentry and A. Jones, J. Chem. Soc. Chem. Commun. (1977) 882.
[29] P.T. Moseley and B.C. Tofifld, eds., *Solid State Gas Sensors* (Hilger, Bristol, 1987) p. 17.
[30] S.J. Gentry, in: *Chemical Sensors*, ed. Te Edmonds (Blackie, Glasgow, 1988) p. 259.
[31] Y.Q. Deng, T.G. Nevell, R.J. Ewen, C.L. Honeybourne and M.G. Jones, Appl. Catal. A 101 (1993) 51.
[32] M.G. Jones and T.G. Nevell, Sensors and Actuators 16 (1989) 215.
[33] M.G. Jones and T.G. Nevell, J. Catal. 122 (1990) 219.
[34] R.C. Yeats, J.E. Turner, A.J. Gellman and G.A. Somorjai, Surf. Sci. 149 (1985) 175.
[35] P. Varghese, J.J. Carberry and E.E. Wolf, J. Catal. 55 (1978) 76.
[36] N.A. Boldreva and V.K. Yatsimirsky, in: *Proc. 10th Int. Congr. on Catalysis*, Budapest, 9–24 July 1992, eds. L. Guczi, F. Solymosi and P. Tétényi (Akadêmiai Kiadó, Budapest, 1993) p. 2621.
[37] D.W. Dabill, S.J. Gentry, H.B. Holland and A. Jones, J. Catal. 53 (1978) 164.