

Flammable Gas Detection

THE ROLE OF THE PLATINUM METALS

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There is an obvious need to detect the presence of flammable gases before their concentration levels approach explosive proportions. The platinum metals find application in the three main types of detector developed for this purpose, and each is considered here.

The presence of flammable gases in the atmosphere is a potential hazard in many industrial, commercial and domestic environments. Following the introduction of natural gas as a primary fuel in the United Kingdom during the 1970s, methane is now the most prevalent of the flammable gases in this country. Since it is a product of decaying organic matter it is also found in dangerous quantities in mines, sewers and waste tips. Hydrogen is still a major problem in those countries where it is used as a fuel, and it also occurs as a product evolved from lead-acid accumulators. Liquid petroleum gas (LPG) is used as a portable fuel in a wide variety of applications ranging from heavy industry to leisure caravans and boats. Petrol is an obvious hazard in garages and enclosed car parks. Finally a wide range of hydrocarbons is widely used in the chemical and petrochemical industries.

The hazard posed by a flammable gas is well defined. The concentration range over which the gas in air is flammable can be experimentally determined and the two limits, the lower explosive limit (LEL) and the upper explosive limit are known for most gases (1). It is common practice to seek to maintain the concentration levels below about 20 per cent of the LEL, and the alarm level is usually set at this figure. The LEL for most gases lies between 1 per cent and 5 per cent v/v, therefore any sensor used for monitoring the hazard has to be capable of indicating concentrations in this range with a discrimination of better than 10 per cent of the LEL.

A number of sensors have been developed for

measuring flammable gas concentrations. This paper will deal with the three main types, in all of which the platinum group metals play a central role. The sensor which dominates the field is the calorimetric or catalytic type, often known as the "pellistor"; in this the flammable gas is oxidised on a catalytic surface and the concentration determined from the quantity of heat released in the reaction. This type of sensor is widely used for quantitative measurement of the hazard, and since its introduction (2) in the early 1960s it has had a major effect on working practices and conditions in many industries.

The second type of sensor is based on electrical conductivity changes induced by gas adsorption on metal-oxide semiconductors. This is used primarily as a qualitative indicator of the presence of a gas, or of a change in its concentration. This type of sensor is extensively used, particularly in situations where low concentrations of a wide range of gases need to be indicated. Platinum group metals are used in these devices as an additive to the oxide; their catalytic properties can improve sensitivity and, to some extent, selectivity.

The third type of sensor in which the gaseous analyte interacts with a platinum group metal surface is the catalytic field effect transistor (FET). Dissociation of hydrogen and some hydrogen-containing gases on the catalytically active gate affects the electrical characteristics of the FET by an amount proportional to the gas concentration. As yet, these sensors have not made a major impact in the market place, but they are likely to do so in the future because

they are silicon-based devices and thus lend themselves to microfabrication techniques.

Calorimetric Gas Sensors

The calorimetric device operates on the principle of detecting the heat evolved during the combustion of flammable gas in ambient air. The total oxidation of methane, for example, liberates 803 kJ/mol of heat. If, under the conditions of measurement, the rate of reaction is dependent on the concentration of the fuel then determination of the heat evolved provides a means of measuring gas concentration. The evolved heat can be measured as a temperature rise, and a catalyst is used in order to achieve an adequate temperature rise (rate of reaction) at a conveniently low temperature. Thus the basic constituents of a catalytic calorimetric gas sensor are a temperature sensor, a catalyst and a heater to maintain the catalyst at the operating temperature.

The simplest form of sensor, used in many early instruments, is a platinum coil which acts as sensor, catalyst and heater. However bulk metallic platinum is a relatively poor catalyst for hydrocarbon oxidation. Hence the element must operate at a high temperature—about 1000°C for methane—which reduces its lifetime because of metal evaporation. The most significant improvement in the lifetime of the sensor has resulted from the use of more active catalysts, so allowing the operating temperature to be reduced considerably. Separation of the catalyst and the heater allows catalysts with a larger surface area, and hence greater activity, to be employed.

The most active catalysts for oxidation reactions are palladium, rhodium, platinum and iridium. This is because conditions on their surfaces are at an optimum for the reaction between fuel and oxygen. The heat of adsorption of the reactants is low enough to reduce the activation energy for oxidation, yet sufficiently high to ensure an adequate surface coverage (3, 4). Gold is inactive as a catalyst because oxygen is adsorbed only very weakly, thereby resulting in too low a coverage. Transition metals adsorb oxygen too strongly, which results in a high ac-

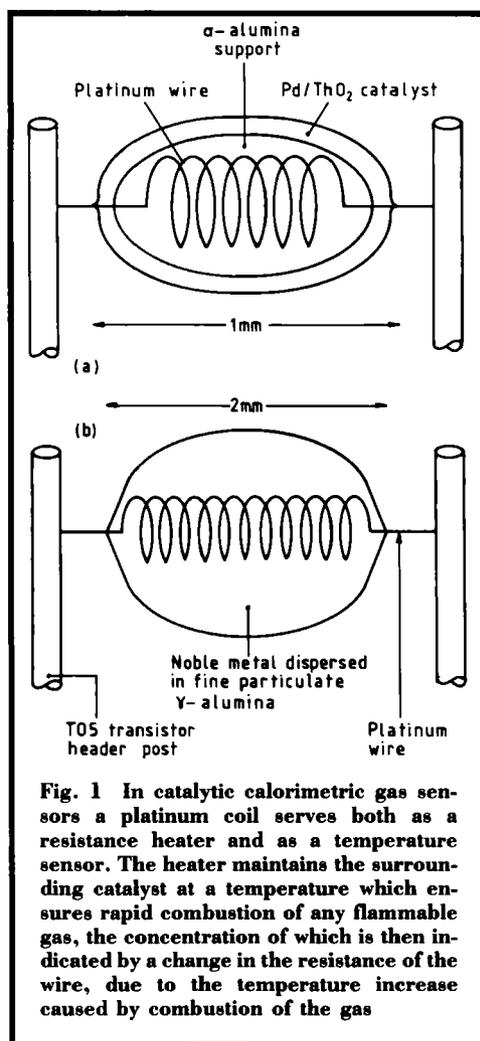
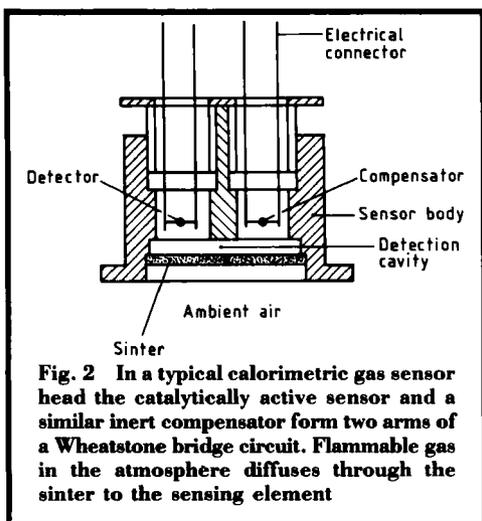


Fig. 1 In catalytic calorimetric gas sensors a platinum coil serves both as a resistance heater and as a temperature sensor. The heater maintains the surrounding catalyst at a temperature which ensures rapid combustion of any flammable gas, the concentration of which is then indicated by a change in the resistance of the wire, due to the temperature increase caused by combustion of the gas

tivation energy for oxidation and in extreme cases they can form bulk oxides. This emphasises the suitability of platinum metal catalysts at the elevated temperatures required for oxidation of the flammable gas. Moreover palladium and rhodium are more active than platinum for the oxidation of methane, catalysing the reaction at around 500°C. The form of the "pellistor" device is shown in Figure 1(a). It consists of a platinum coil encapsulated in alumina, which is coated with catalyst (2). Platinum is used as a resistance thermometer because of its high temperature coefficient of resistance and coils can be easily made. The coil



also serves as a resistance heater. Typically a coil consists of about 10 turns of 0.05 mm diameter wire forming a helix having a length of 1 mm and a diameter of 0.5 mm.

In the commonest arrangement a catalytically active sensing element and a similar but catalytically inert compensator element form two arms of a Wheatstone bridge circuit (1). Power is supplied to the circuit to heat the elements to their operating temperature; the values of the fixed resistors, arranged in parallel with the elements, are chosen to balance the bridge in air. The out of balance voltage, resulting from the presence of flammable gas, is dependent on the change in temperature, which in turn is dependent on the rate of reaction and the partial pressure of the flammable gas. This and similar types of sensor are widely used in various kinds of flammable gas detection instruments, which may be hand held or fixed installations. Gas usually reaches the sensing element by diffusion through a sinter exposed to the atmosphere in a typical configuration shown in Figure 2. The effect of temperature on the out of balance voltage and on the power drain of a typical sensing element is shown in Figure 3. Also shown is the current required to attain the temperature when the room temperature resistances of the detecting and compensating elements are about 1.3Ω, each.

At high temperatures the rate (signal) is less dependent on temperature and is limited by the mass transport of fuel across the sinter to the sensing element. Under these conditions the rate is independent of the chemical nature of the catalyst and only geometric factors such as separation of the element from the sinter influence the signal (5). The mass-transport-limited (MTL) mode of operation has the disadvantage of increasing the response time to several seconds but confers several advantages:

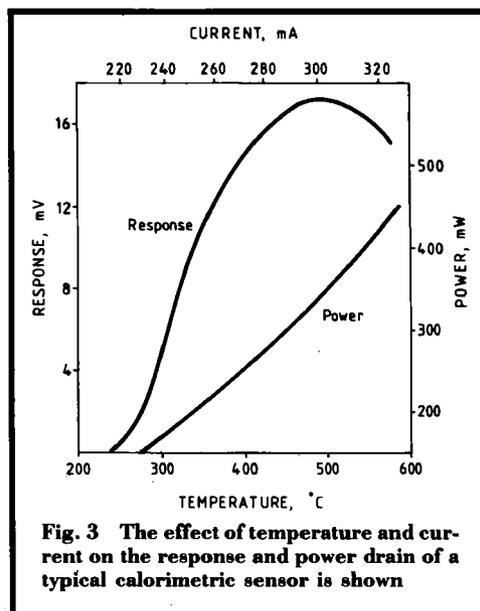
Small variations in the catalytic activity of the elements do not affect the signal.

Minor voltage (hence temperature) fluctuations do not influence the signal.

The rate of diffusion and hence the response is linearly dependent on the flammable gas concentration.

A direct, approximate measure of flammability (per cent LEL) is obtained which is largely independent of the gas or gases present.

Thus, an instrument calibrated to read 0 to 100 per cent LEL in a standard fuel will provide an approximate estimate of the explosiveness of any vapour or mixture of vapours. If the composition of the fuel-air mixture is known then simple correction factors



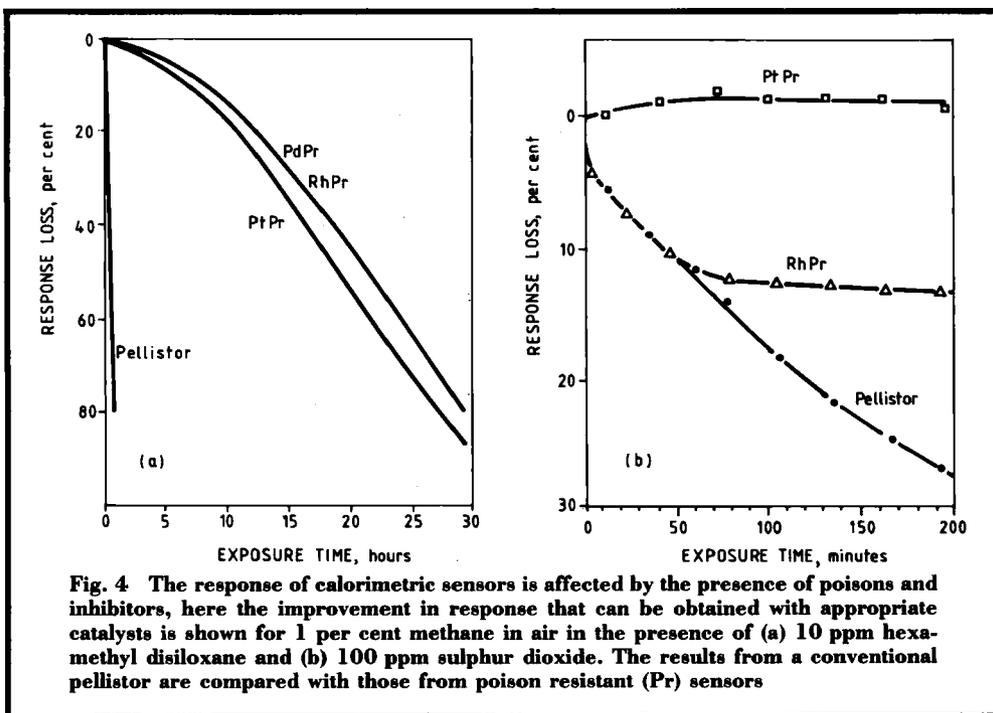


Fig. 4 The response of calorimetric sensors is affected by the presence of poisons and inhibitors, here the improvement in response that can be obtained with appropriate catalysts is shown for 1 per cent methane in the presence of (a) 10 ppm hexamethyl disiloxane and (b) 100 ppm sulphur dioxide. The results from a conventional pellistor are compared with those from poison resistant (Pr) sensors

may be applied to produce more accurate measurements (1). The use of platinum metal catalysts therefore permits operation in the mass transport limited region, with its many advantages, at comparatively low catalyst temperatures.

The major limitation of catalytic calorimetric gas sensors is their loss of sensitivity on exposure to atmospheres containing poisons (which have an irreversible effect) and inhibitors (which have a reversible effect). Common examples are silicones, alkyl lead compounds, phosphate esters, halogenated compounds and sulphur-containing compounds. In the presence of these species a low measure of the concentration of flammable gas is obtained. One solution to the problem is to incorporate a filter, for example activated charcoal, to remove the offending vapour. However charcoal filters will also adsorb higher hydrocarbons and this limits their use to methane, ethane, carbon monoxide and hydrogen. This has led to the development of sensing elements which are much more resis-

tant to poisons than the conventional devices. They generally take the form of a platinum coil surrounded by a porous bead comprising the platinum metal catalyst dispersed throughout a support having a high surface area, such as γ -alumina (6), as shown in Figure 1(b). Improved poison resistance is achieved through:

- [a] Dispersion of the platinum metal throughout a porous support, which increases the effective surface area available for reaction. Under MTL conditions increasing the intrinsic activity of the catalyst — that is the activity which would occur in the absence of mass transport control — effectively produces more “spare” surface, resulting in a lower apparent rate of poisoning.
- [b] Utilising a catalyst having a high intrinsic resistance to poisoning; for example in methane detection platinum is less susceptible to inhibition by hydrogen sulphide or sulphur dioxide than either palladium or rhodium.

Since platinum is intrinsically less active than

palladium or rhodium the relative resistance to poisoning will be determined by the relative importance of factors [a] and [b] above. The improvement achieved using these catalysts is shown in Figure 4 which illustrates the effect of hexamethyl disiloxane (poison) and sulphur dioxide (inhibitor).

Poisons may deactivate different reactions at different rates. On non-porous catalysts, site heterogeneity may result in some reactions occurring on sites that are more easily poisoned than others (7). For porous catalysts the poisoning rate may vary with the relative rates of adsorption and diffusion of the poison, and reaction and diffusion of the reactants. It has been found that in order to minimise inhibition of methane oxidation (slow reaction, fast diffusion) by halogenated or sulphur-containing gases the type of platinum metal is as important as the physical properties of the catalyst, such as dispersion and porosity (6). For silicone, lead and phosphorus poisons the increased dispersion and porosity of the catalyst, rather than the type of platinum metal, provide the best means of increasing the poison resistance of the sensing element. For butane oxidation (fast reaction, slow diffusion), the differences in the behaviour of the platinum metals in halogenated and sulphur-containing gases are less significant than for methane oxidation. However for the poisons the behaviour in butane follows a similar pattern to that in methane (6). It is apparent from the above discussion that the design of poison-resistant elements has strong parallels with catalyst design in the automotive and petrochemical industries. However, because of the considerably smaller scale of use of platinum metals in gas detection, the effectiveness of the catalyst is not as important, therefore effort can be concentrated on maximising poison-resistance.

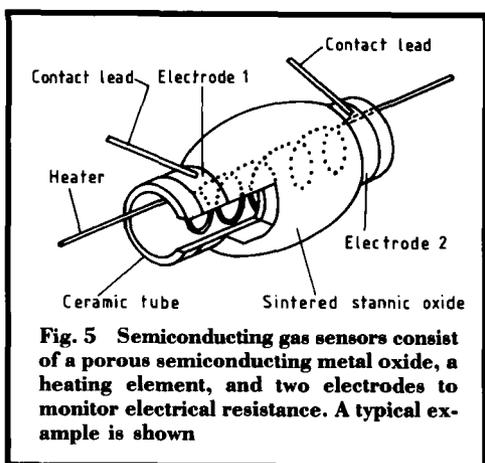
Another phenomenon, catalyst coking, can also adversely affect the performance of catalytic elements. Here carbon is deposited when the dehydrogenation rate of the fuel becomes appreciable at very high concentrations, for example >20 per cent methane in air. Surface carbon may poison the oxidation reac-

tion, and larger deposits change the physical size, morphology and, to a lesser extent, emissivity of the element (8). All these factors alter the power dissipated by the calorimeter and thus change the sensor output. Even when carbon is subsequently burnt off in air permanent damage to the element may occur, indicated by a change in the zero level of the sensor. The incorporation of thoria with palladium in the "pellistor" alleviates this problem. The role of thoria is to disperse the palladium which is present only in metallic form after exposure to the reducing atmosphere, when methane concentrations are greater than 10 per cent (9). This reduces the rate of sintering and thus the formation of large metal particles on which coke would preferentially be formed. Thus increased dispersion of platinum metals provides resistance to coking as well as to catalyst poisoning and inhibition.

If the concentration of oxygen is too low for complete oxidation to occur then the measured signal will be lower than that obtained when the oxygen concentration is at normal levels (approximately 21 per cent). Thus the sensor reading may be ambiguous at high concentrations of gas in air, which are then falsely indicated as being below the LEL; for methane this range is 40 to 100 per cent (10). One method used to overcome this problem is to employ a separate transducer, again calorimetric in nature, within the same instrument, which utilises the difference in thermal conductivity of flammable gas and air.

The rate of development in the field of calorimetric sensors has slowed down in the last few years following the development of poison-resistant elements. Currently attention is focused on the following areas, listed in approximate order of importance:

- [i] reducing the power drain of the sensor,
- [ii] increasing further the long term stability and poison-resistance of the sensor,
- [iii] providing advance warning of poisoning,
- [iv] increasing the sensitivity,
- [v] reducing the response time,
- [vi] providing some degree of selectivity between different fuels.



The successful operation of any catalytic calorimetric sensor depends crucially on the performance of the catalyst. New catalysts having increased activity, stability, poison resistance and selectivity would influence areas [i], [iii], [iv] and [vi] above. There is however, little development work taking place in this field. Attention is confined to miniaturisation (area i), utilising microprocessor technology for interrogation of the sensor at different temperatures (areas iii and vi) and developing more sensitive thermal sensors, for example pyroelectric materials (11) (areas i and iv).

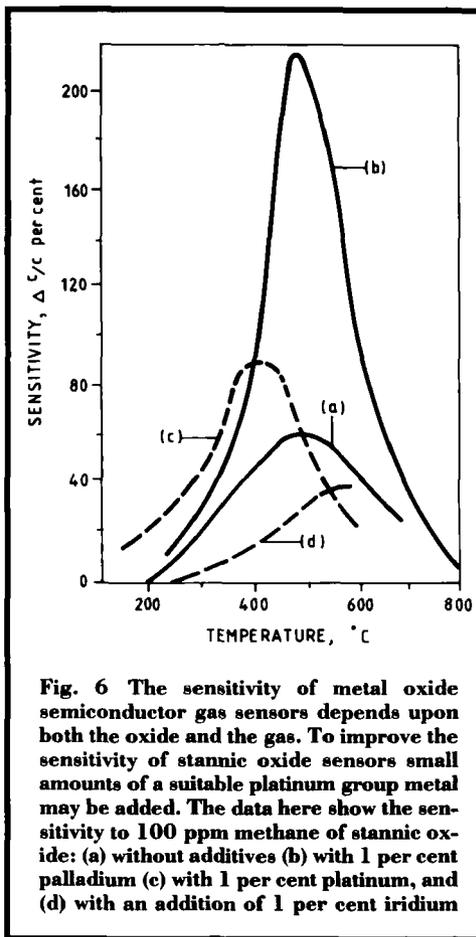
The catalytic calorimetric gas sensor, as demonstrated by its widespread use throughout industry, has proved to be a reliable means of measuring flammable gas concentration or explosiveness of a gas mixture in air. Poison-resistant devices have reduced the problems of operation in poisonous environments thus extending the usefulness of these sensors.

Metal Oxide Semiconductor Gas Sensors

It has long been known that the electrical conductivity of many semiconductors is changed when some gases adsorb on the surface, and that this effect can be reversible. This forms the basis of some widely used gas sensors. A typical form of sensor is shown in Figure 5. General models have been developed which satisfactorily explain the mechanisms underlying the ma-

ior effects (12, 13) but some of the more detailed behaviour still requires elucidation. It is however clear that, in most instances, the interaction of gas with the solid surface is a catalytic reaction involving adsorbed species. Thus metal oxides are particularly suitable for donor gas detection since there is always ionosorbed oxygen on the surface, associated with the defects caused by non-stoichiometry in the solid. These defects are also the source of free electrons contributing to the electrical conductivity. Therefore interaction with the adsorbed oxygen affects the conductivity and in an oxygen rich atmosphere (air) the effects will be reversible.

A number of papers have reviewed studies related to this type of gas sensor, for example



see (14, 15). The major attraction of these devices is that they are very sensitive; concentrations below 1 ppm of some gases can be detected (16). The major limitation is that they are almost completely non-selective and, unlike calorimetric sensors, there is no correlation between the indication obtained and the explosibility of the gas. This is the major reason why these devices have not been used to any significant extent for quantitative measurement.

A number of approaches have been explored with a view to improving the selectivity. Different oxides show different sensitivities to different gases and although much of the literature is concerned with stannic oxide and zinc oxide a wide variety of both binary and, more recently, ternary oxides have been studied. The sensitivity of the sensors plotted against temperature gives curves as shown in Figures 6 and 7. The characteristic "volcano" shaped curve is almost universally obtained. As the temperature of maximum sensitivity is different for different gases, a degree of selectivity can be achieved by judicious choice of operating temperature.

The third approach which has been widely studied is to introduce additives or promoters into the oxide in order to change either the electrical characteristics or, more importantly, the chemical nature of the surface. The addition of promoters to catalysts in order to increase their activity or selectivity is a well tried technique in catalysis. The promoters achieve this by increasing the coverage of reacting species or by easing the route for either reaction or desorption. The introduction of foreign cationic species, of different valency to that of the parent cation, into the lattice of a metal oxide can markedly affect the availability of free electrons, and thus can have a large effect on the conductivity. The indications from current understanding are that this would have a general effect on all gases adsorbing on the surface and would not necessarily achieve the desired effect of enhancing the adsorption or the reaction of any particular gas. If, on the other hand the additive is at the surface and af-

fects the catalytic activity of the surface, this could have the effect of enhancing the oxidation reaction and the consequent electronic effect of one gaseous species relative to another. Many metallic species have been introduced into oxides in attempts to do this. Most success has been achieved with the known oxidation catalysts, in particular the metals of the platinum group, although some success has also been reported with other metals such as silver (17). Commercially available metal oxide flammable gas sensors consist of stannic oxide with one or more of the platinum group metals added at a concentration of around 1 per cent w/w.

Although this approach is widely used the processes involved are not well understood and the advances made have been achieved empirically. One important process may be preferential adsorption onto the additive site at the surface and subsequent spillover onto the oxide surface thus causing a conductivity change (12, 18). Very strong adsorption onto the additive would, on this basis, inhibit the reaction, although this is a simplification of what must be a complex process. Evidence of

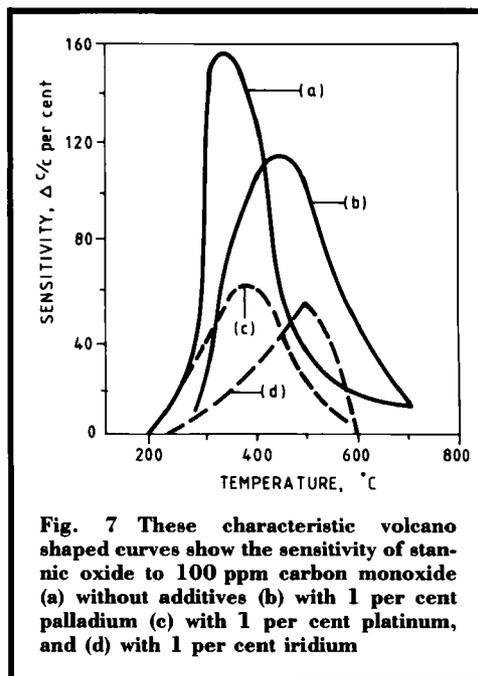
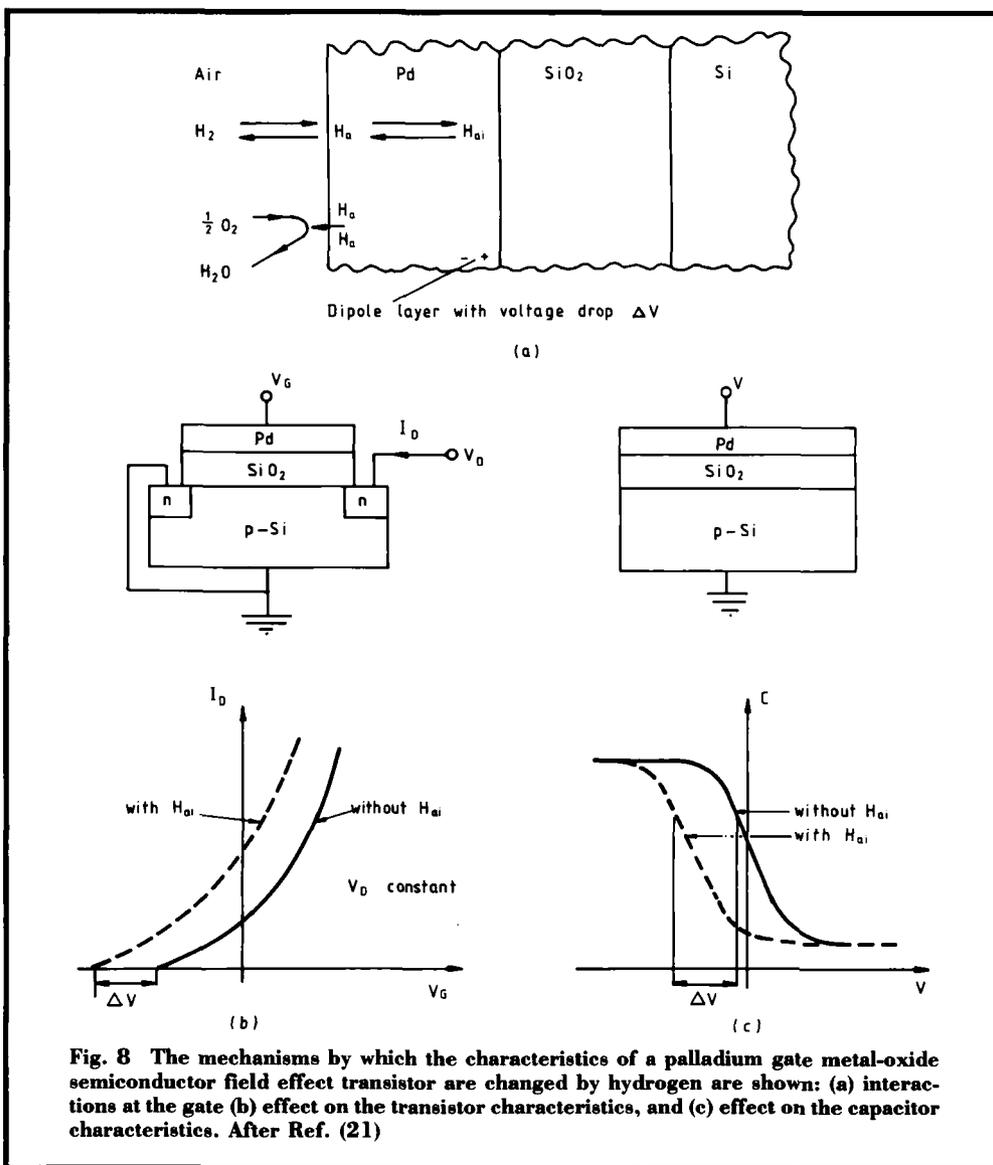


Fig. 7 These characteristic volcano shaped curves show the sensitivity of stannic oxide to 100 ppm carbon monoxide (a) without additives (b) with 1 per cent palladium (c) with 1 per cent platinum, and (d) with 1 per cent iridium



complexity is the observation that known metallic catalyst behaviour is not directly transferable to the oxide/additive system; good catalysts for the oxidation of a particular gas do not necessarily improve the sensitivity of an oxide to that gas when they are used as additives. A more appropriate criterion is perhaps the adsorption properties of the additive. It is well known that the properties of catalysts are very dependent on the catalyst support material,

hence the above observation is not altogether surprising. Figures 6 and 7, show the effect of platinum group metal additives on the sensitivity of stannic oxide to methane and carbon monoxide, respectively. Although palladium metal is an efficient oxidation catalyst for both gases, its addition significantly enhances sensitivity to methane but reduces sensitivity to carbon monoxide. It is suggested that palladium produces a route for the dissociative

adsorption of methane, with subsequent spillover of adsorbed species onto the stannic oxide. This increases the surface concentration which is intrinsically low on the undoped oxide and leads to greater sensitivity to the gas. On the other hand the high coverage of carbon monoxide, which is more easily dissociated on stannic oxide, is relatively unaffected by the addition of palladium. The effect of platinum is not as marked in terms of the sensitivity to methane, but it has the effect of significantly reducing the temperature of maximum sensitivity. However, platinum reduces the sensitivity to carbon monoxide which may imply that carbon monoxide is adsorbing more strongly on platinum than on stannic oxide.

There is a wealth of catalysis literature relating to the platinum group metals and metal oxides which might be tapped in the search for selective detection materials. A fundamental difference, however, between catalytic studies and sensor work selectivity relates to the adsorbents or reactants. The full potential of this type of sensor is still far from being realised, perhaps more in terms of toxic rather than flammable gas measurement. However the catalytic metals will play an important role in combination with a range of metal oxides in producing a number of sensors suitable for a variety of applications.

Catalytic Gate Field Effect Transistor Gas Sensors

The first hydrogen sensitive metal-oxide semiconductor (MOS) field effect transistor was described by Lundström in 1975 (19, 20). Since then this type of device has attracted considerable attention but as yet the commercial impact has been slight. The mechanism by which the presence of hydrogen in the atmosphere affects the characteristics of MOS devices has been explained by Lundström and his co-workers in terms of dissociation of molecular hydrogen to atomic hydrogen on the palladium surface (21). Atomic hydrogen diffuses into the metal film and adsorbs on the in-

ner palladium surface, as shown in Figure 8(a). The adsorbed atoms form dipoles at the metal-insulator interface, resulting in an increase in the work function of the metal at the interface. This in turn affects the threshold voltage (the voltage at which the inversion layer starts to form) of the transistor, or the flat band voltage if the device is in the form of a capacitor. The net result of the dipole layer formation is to generate an extra voltage in series with the externally applied voltage, thus shifting the device characteristics as shown in Figure 8(b) and 8(c). The change in the work function is assumed to be proportional to the interface concentration of adsorbed hydrogen, so that the maximum change will occur when every interface site is occupied by a hydrogen atom. Measurable changes can be obtained for very low concentrations (<1 ppm) of hydrogen in some instances.

The hydrogen coverage at a given hydrogen pressure depends on two processes. One is dissociation and subsequent sorption into the palladium film; the second process is the mechanism whereby the hydrogen desorbs. The latter controls the rate of recovery of such a sensor and takes place through recombination to form molecular hydrogen in vacuum or inert gas, or through water formation in the presence of oxygen. When the competing processes balance, the hydrogen coverage is at a steady state. This in fact leads to a considerably higher sensitivity in an inert atmosphere than in air, since the probability of water formation is much higher than that of spontaneous recombination.

The catalytic metal has three major roles in these sensors, it dissociates the analyte gas through catalytic action, it transports hydrogen atoms to the metal-insulator interface and it adsorbs the hydrogen atoms at this interface as detectable dipoles. First hydrogen molecules, hydrogen sulphide molecules and others are dissociated to form hydrogen atoms, a process which is catalysed efficiently by the platinum group metals. Other metals, or metal oxides such as palladium oxide, may also be employed. The metal also catalyses other reactions, such

as the oxidation of hydrogen by oxygen or chlorine, or the oxidation of hydrogen sulphide by oxygen. The second role of the metal is to allow transport of the hydrogen atoms through the metal layer. Hydrogen is unique in this respect, because the hydrogen ion is a bare proton and thus much smaller than any other ion or atom. Diffusion of hydrogen atoms is fast in most metals including the platinum metals. The high solubility of hydrogen in palladium, however, makes this system unique. If the gate is fabricated of a porous metal layer then any gas can diffuse directly through the pores in the layer even without catalytic dissociation. The same applies when the gate consists of a non-continuous metal film such as a grid. However, some charge exchange must occur to provide the dipole layer at the metal-semiconductor interface. This is the third role of the metal layer which is to adsorb the diffused atoms or molecules as dipoles at the metal-support (insulator, semiconductor) interface. The dipole layer formed changes the semiconductor surface field experienced by the semiconductor. Thus a surface-field sensitive device such as a MOS capacitor, MOS transistor or a Schottky diode generates a signal from this field change.

In practice this type of device is used for hydrogen detection in air and other environments, particularly for hydrogen leak detection. The operating temperature is usually in the region 60 to 150°C; elevated temperatures being necessary to reduce the response time and to avoid water adsorption, although for the palladium/hydrogen system room temperature operation is possible. The device can also be used for hydrogen sulphide and ammonia detection where presumably both gases dissociate at the surface. Hydrogen sulphide does not poison the catalyst in air but does so in an inert atmosphere. Not all the devices utilising a palladium gate respond to ammonia; the reasons for this are differences in the structure of the metal films and the properties of the insulator surfaces. Limited success has been achieved using different catalytic metals particularly platinum, iridium and lanthanum as the gate material. A number of dif-

ferent gate structures have also been investigated. Porous palladium films have been used in devices sensitive to carbon monoxide, ethanol and some other hydrocarbons (21).

One of the problems with these devices is the temperature limit determined by the silicon. A number of investigations have explored the possibilities of the "floating gate", that is a gate in grid form which is physically separate from the silica layer (22). Despite these different approaches this type of device is still limited in application to hydrogen, hydrogen sulphide, ammonia and a number of the more reactive hydrocarbons. The device cannot be used as an explosimeter, as is the case for the calorimetric sensor, or as a general indicator of almost any flammable gas, as is the case for the metal oxide sensors, but because of the limited interference it may be possible to use it to monitor for single components in some atmospheres. Its high sensitivity in air and inert backgrounds, ease of fabrication and compatibility with microelectronic systems ensures that this type of device will have a significant role to play in flammable gas detection.

Conclusions

All three types of flammable gas sensor considered in this paper involve reactions between the analyte, which is usually a reducing gas, and a solid surface. The reactions which take place are governed by the nature of the surface, and each of the three types of sensor described depend on the unique adsorption properties of the platinum metals. This, however, is manifested in different ways. The calorimetric sensor relies on the catalytic activity of the metal to promote the oxidation of the analyte on the sensor surface. The role of the metal in the resistive semiconductor is to enhance the surface activity with respect to certain gaseous species. In the field effect transistor sensors the role of the metal is to dissociate the analyte at the surface and to allow the formation of a dipole layer at the metal/insulator interface. Thus, the platinum metals have been, and will continue to be, central to the development of improved sensors for flammable gas detection.

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Superconductivity in Platinum Compounds

A review summarising the published data on the superconductivity of platinum group metal compounds was published here in 1984 (1), and since then efforts to understand and develop superconducting materials have continued.

Last year some 390 scientists from twenty countries met in Sendai, Japan, for the Yamada Conference XVIII on Superconductivity in Highly Correlated Fermion Systems, and the proceedings have now been published (2).

Materials containing five of the platinum metals were considered; the exception being osmium, although it is known that high purity osmium and several osmium-containing compounds are superconductors. Of the fifteen contributions that dealt, at least in part, with the platinum metals, six were concerned with the system UPt_3 . Recent developments were reviewed by H. R. Ott, antiferromagnetic ordering has been achieved in UPt_3 by replacing platinum with palladium or gold, or by substituting thorium for uranium. These systems were included in an overview of work on magnetic fluctuation and order, by G. Aeppli. The specific heat and the resistivity of $(U,Th)Pt_3$ were considered by K. Kadowaki. The compound UPt_3 was one of several whose normal ground state properties were investigated by B. Renker, while V. Müller reported the results of ultrasonic attenuation experiments on the same material. Using

polarised light scattering S. L. Cooper examined single crystals of UPt_3 and URu_2Si_2 . Normal and superconducting properties of the latter were reported by Y. Onuki, while a contribution from H. Iwasaki considered superconducting and heavy-fermion behaviour in the $(La_{1-x}Ce_x)Pd_2Ge_2$ system.

The three pseudoternary systems $Ho(Rh_{1-x}Ru_x)_4B_4$, $R(Rh_{1-x}Ru_x)_4B_4$ and $R(Rh_{1-x}Co_x)_4B_4$ were the subjects of contributions by H. Adrian, H. Iwasaki and H. C. Ku, respectively. In addition thermal expansion measurements on the magnetic superconductor $Er_{0.4}Ho_{0.6}Rh_4B_4$ were given by R. Villar, while Y. Koike reported the effects of strain on superconducting and ferromagnetic transitions of $ErRh_4B_4$. The superconducting and magnetic properties of $CeRh_4B_4$ and $PrRh_4B_4$ were reported by K. Kumagai, and evidence for triplet superconductivity in $LuRu_4B_4$ was presented by A. Sulpice.

Regrettably, it is not possible to give here the names of the 63 people who co-authored the papers noted; readers are strongly recommended to refer to the published proceedings.

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