Surface Modification of Solid State Gas Sensors

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Abstract

The phenomenon of electrical conductivity being controlled by the chemical state of a surface grafted reactive centre, resulting in a room temperature gas response, is demonstrated. The reactive centres can be chosen to be specific to a particular gas, providing a route to new types of gas detectors tailored for a particular application. Generalization of the phenomenon was verified. Surface grafting of Ti, Ru and Pt centres onto SnO$_2$; Ti and Pt centres onto TiO$_2$; and Pt centres onto BaSn$_{0.97}$Sb$_{0.03}$O$_3$ resulted in a room temperature gas sensitivity specific to each system.

Surface grafting of Ru centres onto SnO$_2$ resulted in additional electronic states in the SnO$_2$ band gap associated with surface Ru species, revealed by XPS and correlated with resistance increase of the material. An electronic interaction between grafted Ru centres and the SnO$_2$ support was manifested in conductivity being controlled by the surface state of the Ru. Variations in the chemical state of the surface grafted Ru caused by gas chemisorption were revealed by XPS and this was correlated with conductivity change measured as gas response of the device at room temperature. The samples were characterized by EXAFS to confirm the structure of the surface Ru species, TPD, UV-visible spectroscopy, XPS and electrical measurements. DFT molecular cluster calculations were also performed to ascertain the origin of the gas response.

The mechanism of the room temperature CO response of SnO$_2$ decorated with small Pt particles was refined. In this case Pt was applied by common impregnation techniques. The conductivity was shown to be controlled by the surface state of the Pt. The CO response at room temperature was found to be specific to the presence of Pt(II) species. The mechanism was assigned to CO chemisorption onto Pt(II), resulting in charge transfer, measured as conductivity increase. The samples were characterized by XPS, TPD, SEM, mass spectrometry and electrical measurements. Comparison of the results presented for Pt decorated BaSn$_{0.97}$Sb$_{0.03}$O$_3$ and BaFeO$_3$ demonstrated the phenomenon to be general providing that Pt particles act as surface traps, controlling the conductivity.
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Chapter 1. Introduction.

1.1 General.

Various chemical pollutants and odorous components, such as CO, H₂S, Cl₂, CO₂, NO₃, SO₂, natural gas (CH₄), propane (C₃H₈), flammable organic vapors and so on, emitted from industries, car exhausts and faulty domestic appliances into the atmosphere have been creating hazardous, environmental and health problems. The recent emergence of concern over global environmental issues has stimulated substantial research and development in the field of gas detection and monitoring devices. The health and safety regulations require detection of inflammable and toxic gases in the atmosphere at very low levels, measured in terms of parts per million [1]. Unlike a detector of an analytical instrument, a gas sensor is required to operate at various locations in situ, hence the growing necessity for reliable miniaturized systems able to produce an electrical signal corresponding to concentrations of minor constituents of an atmosphere.

Solid state gas sensors utilizing semiconducting metal oxides as sensitive elements provide an attractive solution to monitoring and detection problems, being of light and simple construction. The principle of operation of metal oxide based sensors involves a change in the surface conductivity of the semiconducting oxide at elevated temperatures upon gas chemisorption. Provided the semiconducting oxide is presented in a high-surface-to-bulk form, the electronic consequences of the solid-gas interactions, which are confined to the surface layer, are manifested throughout a considerable volume of the solid and the material respond to variations in the atmospheric composition by changes in electrical conductivity. Semiconductor sensors are devices operated around 400°C, that consist of a sintered finely porous metal oxide layer deposited onto a ceramic substrate, which includes a heating element and a pair or two of electrodes. These devices offer high sensitivity, fast response, possibilities of miniaturization and are simple, robust and inexpensive.
Many metal oxides, such as SnO₂ [2-4], ZnO [5,6], TiO₂ [7], WO₃ [8], ternary metal oxides particularly the perovskites BaSnO₃ [9] and BaTiO₃ [10]; and complex metal oxides [11-13] have been examined for gas sensing. Tin dioxide has to date by far been the material of choice due to its high sensitivity and relatively low operating temperature [4,14]. Due to its wide application as an active element in a sensor technology, SnO₂ has become a kind of model system in numerous empirical and scientific research studies of the mechanism by which metal oxides function as gas sensors and of the potential for enhancing their performance.

The major disadvantage of the semiconductor gas sensors developed so far is the lack of stability and selectivity. Strong cross sensitivity of nearly all metal oxides towards gases of similar chemical properties and towards humidity in air at elevated temperatures is a strong drawback in the practical application of semiconductor sensors. Furthermore, the need to operate sensors at relatively high temperatures, 300-400°C, requires inclusion of a heater in the device and a subsequent power drain. Evidently, due to a significant power consumption it is not possible to drive the device by a battery. Nowadays worldwide research efforts are devoted mostly to resolve the issues of long term stability and selectivity of metal oxide sensors and to lower the operating temperature.

Operation of semiconducting metal oxides as gas sensitive elements involves gas recognition, through chemical interaction of the reactive gas with the oxide surface, and subsequent transduction of what is recognized into a sensing signal, through variations in the electrical conductivity of the material. Since semiconductor sensors depend on reactions of gas molecules at oxide surfaces there is strong parallel between their function and the mechanism of heterogeneous catalysis. The chemical optimization of the sensor performance is therefore performed by modification of the oxide surface with catalytic metal additives to induce the surface reactions at lower temperatures. Decoration of the oxide surface with metal additives like Pt [15-17], Pd [16,18], Ag [19], Au [15] is known to promote both selectivity and sensitivity and to lower the operating temperature.

The chemical sensitivity of a semiconducting oxide surface serves as a way to transduce the chemical information around the surface into an electrical signal; the actual quality of the
signal is defined by the transduction properties of the sensor material. Hence the chemical optimization of the sensor performance would be necessarily combined with the physical optimization based on optimization of the transducer function. The latter is largely dependent on technological factors such as microstructure of the base material and the structure and geometry of the sensor device. The trends in current research and development include:

- controlling the sintering procedures of the oxide materials, with the use of specific additives to control grain size and porosity; [20]
- improving the common ceramic fabrication technologies with particular emphasis on thick- and thin-film processes; [21, 22]
- modifying the contact geometry of the devices to exclude or modify specific contributions to the overall conductance changes; [23, 24]
- choosing a specific operation temperature for the particular detection of certain compounds; [25]
- operating in the AC mode at different frequencies; [26]
- operating with modulated temperatures; [27]
- using sensor arrays or modulated sensor outputs, applying subsequent pattern recognition [28, 29].

In some particular cases [30, 31] of sintered porous SnO₂ body decorated with fine Pt or Pd particles, the catalyst-modified gas-sensitive electrical conductivity was induced at room temperature. This particular effect was shown to be due to the actual conductance response mechanism being modified. The sensor operation in this case was based on the gas recognition through a specific interaction of the target gas with the supported noble metal particles, for which the semiconducting oxide polycrystalline porous body served as a transducer. This particularly interesting and practically useful phenomenon, if fully understood and exploited, can lead to development of the gas sensitive devices operating at room temperature with the possibility for promotion of selectivity by the choice of surface metal additives.
1.2 Basic phenomenon of gas sensitivity in heated metal oxides.  
1.2.1 Electronic structure and conductivity.

For the purpose of detection of minor concentrations of noxious gases in air (at fixed partial pressure of oxygen) metal oxides are most commonly used in a form of finely porous sintered ceramics with submicron grain size [32] (Fig 1.1).

![Figure 1.1](image.png)  
*Figure 1.1 Scanning electron micrograph of the sintered structure of a conventional Cr$_{1.8}$Ti$_{6.2}$O$_{3}$ sensor (our results).*

The overall conductivity in polycrystalline samples contains contributions from individual crystallites, grain boundaries, the insulating parts (like pores) and the contacts [4]. To a single crystallite the band theory of solids [33] can be applied to describe its semiconducting properties. In a semiconductor the valence electrons, originating from the outer electronic shell of constituent atoms, are delocalised and the electronic states extend throughout the whole of a solid. The energy levels of the delocalised electrons in the crystal fall into well defined energy bands, rather than the discrete levels found in atoms. The top filled energy band formed of the closely spaced bonding crystal orbitals is called the valence band. The next empty energy band, formed by closely spaced antibonding crystal orbitals is separated from the valence band by a substantial forbidden energy gap and is called the conduction band.
In practice, due to a small crystallite size and high concentration of surface defects, localized energy levels termed intrinsic surface states are formed within the forbidden energy gap. Intrinsic occupied donor states, positioned below the bottom of conduction band are induced due to oxygen deficiency, (oxygen vacancies, $V_O$) [34]. Defects due to metal deficiency (metal vacancy, $V_m$, oxygen interstitials, $O_i$) yield the formation of empty surface acceptor levels above the valence band. Electrical conduction arises due to ionization of intrinsic donors/acceptors, which leads to electron excitation from donor states to the conduction band or from the valence band to the acceptor states. The Fermi energy position within the solid depends on the energy distribution and the ionization of the defect levels [33]. An n-type semiconductor has a higher density of states in the conduction band. The Fermi level, or the chemical potential for the electrons in solid, in this case is expected to lie close to the conduction band. A p-type semiconductor has a majority of positive charge carries, i.e. holes, in the valence band. The Fermi level in this case lies close to the valence band.

In pure SnO$_2$, native donor levels of 0.03-0.034 eV and 0.14-0.15 eV below the conduction band edge result from the single and double ionization of oxygen vacancies [35]:

$$\begin{align*}
[\text{Sn}^{'}_{\text{Sn}}, V_O^{-}, \text{Sn}_{\text{Sn}}^{'}] & \longrightarrow [\text{Sn}^{'}_{\text{Sn}}, V_O^{-}] + n' + \text{Sn}_{\text{Sn}}^{x} \\
[\text{Sn}^{'}_{\text{Sn}}, V_O^{-}, \text{Sn}_{\text{Sn}}^{'}] & \longrightarrow V_O^{-} + 2n' + 2\text{Sn}_{\text{Sn}}^{x}
\end{align*}$$

(1.1)

(1.2)

where $n'$ denotes the negative charge carrier (electron).

It is well established that the electrical conductivity in tin dioxide is due to non-stoichiometry as a result of oxygen deficiency [35-37]. The conductivity is of n-type.

Metal oxide sensors for environmental monitoring operate in air, hence an understanding of their interaction with oxygen is crucial. Thermal desorption studies have been reported [38], where sensors were exposed to oxygen at low temperatures (125K). The temperature was then increased linearly with time and desorbing oxygen was monitored in a mass spectrometer. The different interaction mechanisms were identified as a function of temperature (Fig 1.2):
At the typical temperature of sensor operation, which is about 400°C, oxygen chemisorption dominates and hence oxides adsorb atmospheric oxygen at their surface in a reversible way via a charge-transfer interaction [38,39]:

\[
S + \frac{1}{2} O_2 (g) + n' \rightleftharpoons S (O_2)
\]  

(1.3)

where \( S \) denotes an unoccupied adsorption site and \( n' \) denotes a negative charge carrier. The equation gives an oversimplified picture of the surface reaction, since it may also proceed via \( O^- \) or \( O^{2-} \), with higher temperatures favoring the more highly charged species [40].

Due to the interaction of atmospheric oxygen with the oxide crystal, the electronic structure of the near surface region of the solid is perturbed. Chemisorbed oxygen species form extrinsic surface acceptor states in the forbidden energy gap [39]. Extrinsic acceptor states act as trap states removing electrons from the bulk, which come from ionized donors via the conduction band in the case of n-type materials, depleting the subsurface region of the charge carriers and causing band bending. A parameter that is sensitive to chemisorption as well as to physisorption is the work function \( \Phi \), i.e. the energy difference between the vacuum (\( E_{\text{vac}} \)) and the Fermi (\( E_F \)) level at the surface [41]. These quantities and the electron...
affinity, \( \chi = E_{\text{vac}} - E_C \), are shown schematically in Fig 1.3 for the situation before \((\Phi, \chi, E_{\text{vac}})\) and after \((\Phi' = \Phi + \Delta \Phi, \chi' = \chi + \Delta \chi, E_{\text{vac}}' = E_{\text{vac}} + \Delta \Phi)\) gas adsorption respectively on the n-type semiconductor.

![Diagram](image)

**Figure 1.3** Anionic depletive chemisorption on an n-type semiconductor [41].

Note that

\[
\Delta \Phi = -e \Delta \phi_s + \Delta \chi,
\]

(1.4)

whereby \(-e \Delta \phi_s\) denotes the band bending due to chemisorption with transfer of free electrons and \(\Delta \chi\) the potential step due to physisorption and chemisorption without free particle transfer [41].

In the case of p-type materials surface acceptor states remove electrons from the valence band, resulting in an increase in the charge carrier concentration in the near surface region. Fig.1.4 demonstrates cumulative adsorption of oxygen on nickel oxide (p-type). In the case of p-type materials adsorption of oxygen results in the formation of holes in the valence band. The near surface region thus exhibits a high conductance and it would seem that no band bending occurs [42].
Fig 1.4 Anionic cumulative chemisorption on p-type semiconductor. Extracted from K.J.Laider and McGraw-Hill [42]

Fig 1.5 shows the band structure of the subsurface region of an n-type oxide crystallite in air depleted by the surface states associated with the chemisorbed oxygen. An energy level, $E_s$, introduced by oxygen within the band gap is shown, although there are, of course, different levels related to different oxygen species ($O_2^-, O^-, O^{2-}$) [43].

Figure 1.5 Diagram representing the principal energy states within subsurface region of n-type semiconductor in air. From McAleer et al [44].
The charge stored on the surface in the form of ionized oxygen species is balanced by the space charge layer of the opposite sign, or “depletion layer”, in the subsurface region. A potential difference develops between the surface and the bulk of the grain due to charge separation. The development of this potential difference forms a barrier to further chemisorption of oxygen. The surface oxygen coverage and depletion layer thickness then reach a limit, and the oxygen coverage saturates at a rather low value [45].

The depletion layer is characterized by two parameters, namely the depletion layer thickness, $d_{\infty}$, and the Schottky potential energy barrier, $\Delta \phi_s$. The conductance in the depletion layer is dependent upon the charge stored in the surface states, since both $d_{\infty}$ and $\Delta \phi_s$ are depend on the surface states occupancy by the relationship [45]:

$$d_{\infty} = \frac{N_S \theta}{N_D}$$  \hspace{1cm} (1.5)

$$\Delta \phi_s = \frac{e(N_S \theta)^2}{2 \varepsilon \varepsilon_0 N_D}$$ \hspace{1cm} (1.6)

where $N_D$ is the bulk donor concentration, $N_S$ is the number of the surface states and $\theta$ their fractional occupancy.

The depletion layer width is otherwise known as the Debye length $L_D$ [46]. If the particles are small enough, typically in the region of $L_D$, the electrical conductivity would be controlled by the surface trap states occupancy. In air surface states are associated with ionosorbed oxygen. Based on the assumptions that conduction and surface trapped electrons arise only from ionized donors and that within the depletion layer the donors are completely ionized the depletion layer thickness was estimated to be $d_{\infty} \approx 100$-1nm [44].

The upper limit to the Schottky potential barrier height, $\Delta \phi_s$, is set by the difference in the free electron energy in the solid and the surface state energy [41]. In other words the sorption capacity of an oxide depends on the Fermi level position relative to the surface state energy. By varying the energetic distance between the adsorption level and the Fermi level, the adsorptivity of a given surface with respect to oxygen is expected to change.
We note here in passing that various bulk dopants are used in different ways to adjust the electrical behavior of the parent oxide structures [11,12,47]. The effect of bulk impurity aliovalent dopants is to introduce additional impurity donor/acceptor energy levels within the band gap, inducing variation in the Fermi energy. In addition metals with incompletely filled d- or f-electron shells, such as for example Ni (3d^8), introduce localized electronic states associated with the d- or f- electrons in the band gap [48]. In this case local covalent bonds may be formed on oxygen chemisorption which involve surface atoms only which may leave the free electrons in the conduction band of the semiconductor unaffected. Wide band gap semiconducting oxides with empty (d^0) or full (d^{10}) shells such as TiO₂ or SnO₂ have no surface states of the d electrons in the band gap [48]. These materials are particularly suitable for sensing elements based on variations in conductivity due to electronic charge-transfer on gas chemisorption.

Considerations of the conduction mechanism in finely porous sintered bodies needs to take into account that polycrystalline ceramics are characterized by their unique structure, consisting of crystal grains, grain boundaries, intergranular contacts and pores (Fig 1.6)

![Figure 1.6 Schematic drawing of a typical ceramic microstructure.](image-url)
The gas volume within sintered porous artifacts of the high-surface-to-bulk form represents a large fraction of the sample volume and the electrical consequences of oxygen chemisorption at the free surface and at grain boundaries affect most of the volume due to gas diffusion inside the pores.

In the sintering process necks of different shapes and dimensions are formed between powder particles. There are many theoretical treatments considering the current transport through necks of different diameter [39, 49]. At the junction between the grains of an n-type porous sintered body, such as SnO₂ model system, the depletion layers formed on atmospheric oxygen adsorption constitute Schottky barriers (Fig. 1.7). The Schottky barriers at intergranular contacts dominate the resistance, since the electrons must overcome a substantial energy barrier in order to cross from one grain to the another [50].

![Figure 1.7 Schottky barrier model](image-url)
The Schottky barrier height determines the activation energy for conductance, which is directly related to the charge stored at the surface in a form of ionosorbed oxygen. The conductivity in this case is [44]:

$$\sigma = \text{const} \times \exp\left(-\frac{e\Delta\phi_s}{kT}\right)$$  \hspace{1cm} (1.7)

where $\Delta\phi_s$ is dependent on the surface states occupancy (eqn. 1.6). In air surface states are associated with chemisorbed oxygen species.

A statistical analysis by Moseley et al [51] of the response of a large number of semiconducting oxides gives strong evidence that the conduction mechanism in the n-type materials is determined by Schottky barriers at intergranular contacts. A clear indication is the enormous apparent dielectric constant of n-type porous ceramics. In the course of survey they noted that many sensor materials show an anticorrelation of capacitance and resistance upon change in gaseous atmosphere. If the effect of the atmosphere change is to lower the number of adsorbed negative oxygen species, then the depletion layer width will be reduced, leading to an increase in permittivity and decrease in resistivity.

The conductance mechanism in tin dioxide, as a dominant gas sensor material, has been widely investigated [39,46,52,53]. In general, the conductivity of the n-type porous sintered SnO$_2$ structure is best described as Schottky barrier-limited. McAleer et al [44] pointed out that the behavior of the porous structure is in fact controlled not by interconnections between individual grains but by those between domains or agglomerates of crystallites. The size of each structure domain would be large compared to the depletion layer width, that is the Debye length of the electrons. The conductance was thought to be controlled by Schottky barriers separating domains, each including a relatively large number of crystallites. This particular conduction mechanism is applicable to the n-type finely porous ceramics, as supposed to the p-type materials. Work described in this thesis is concerned with n-type semiconducting oxides, exploiting the above property.
1.2.2 Gas detection model.

The electrical conductivity of finely porous n-type oxide ceramics in air is controlled by Schottky barrier mechanism, with the barrier height determined by the charge stored at the surface in a form of ionosorbed oxygen species [51]. The phenomenon of gas sensitivity of metal oxides to low concentrations of a reactive gas in air at elevated temperatures is explained by variations in the surface states occupancy, and subsequent Schottky barrier height, as a result of catalytic oxidation reaction [36,45]. The equations for the formation of the surface oxygen species and its removal by surface catalyzed oxidation of the combustible gas would be [36]:

\[
\begin{align*}
S + \frac{m}{2} O_2 (g) + e^- & \xrightarrow{k_1} S (O_m^-) \quad (1.8) \\
 mR + S (O_m^-) & \xrightarrow{k_2} mRO + e^- + S \quad (1.9)
\end{align*}
\]

\( e^- \) denotes a conduction electron, \( S \) denotes an empty surface site and \( R \) the reactive gas, present at a very low concentrations in air. \( k_1, k_{-1} \) and \( k_2 \) are rate constants.

The conditions for sensitivity to partial pressure of combustible gas are [54]:

\[
k_{-1} \ll k_2 P_R^m ; k_{1} P_{O_2}^{m/2} \ll k_2 P_R^m \quad (1.10)
\]

which are the conditions for activated chemisorption and desorption of oxygen.

In that regime a combustible gas could perturb the equilibrium surface oxygen coverage in air and would establish a steady state occupancy of the surface sites, dependent on the gas concentration.

The model does not consider adsorption of the reactive gas, \( R \), prior to combustion.

A detailed study of the response model, outlined above was reported by Williams et al [55]. They demonstrated that the model based on the assumption that the reactive gas need not adsorb on the oxide surface prior to combustion was in agreement with experimental results.
The steady state oxygen surface coverage in the presence of combustible gas is less than the equilibrium coverage in air. Electrons trapped on the extrinsic surface states return to the conduction band of the n-type material as the surface oxygen coverage decreases, resulting in a decrease in the surface charge density and the depletion layer width and hence in the potential barrier height. As result, an n-type material responds to the reducing gas in air by a resistance decrease. In p-type materials holes are removed from the valence band on oxygen desorption and the result is an increase in the resistance in the presence of combustible gas. Semiconductor sensors are also known to respond to oxidizing gases and, by reactions analogous to (1.8&1.9) it can be predicted that n-type oxides show resistance increase and p-type oxides show resistance decrease in response to minor concentration of oxidizing gases in air.

The steady state conditions for the process of interaction of the combustible gas with chemisorbed oxygen (eqn. (1.8) and (1.9)) imply:

\[ k_1(1-\theta)P_{O_2}^{m/2} = k_1\theta + k_2\theta P_R^m \]  

(1.11)

where \( \theta \) is the fraction of occupied surface states. However \( (1-\theta) \approx 1 \), as \( \theta \) is low due to the development of a potential barrier for chemisorption. The oxygen coverage (the trap state density) is then dependent on partial pressure of combustible gas:

\[ \theta = \frac{k_1P_{O_2}^{m/2}}{k_1 + k_2P_R^m} \]  

(1.12)

A square root response law has been reported for conductivity dependence on gas concentration [23,54]. This implies \( m=1/2 \), that is that the surface species mediating the gas response is \( O^2 \). On oxygen chemisorption the ionized oxygen species \( O^+, O^2, O^- \) are formed [40]. Williams et al [55] proposed that possible oxygen species can be viewed as surface trap states of different trap depths. The active oxygen species which mediate the conductance response were taken as \( O^2 \). They suggested that these species, whilst present at low concentrations compared to the other charged oxygen species, represented a shallow trap state and therefore controlled the conductivity variations.
1.2.3 Characteristic behavior.

(i) Gas response

The gas detection model, based on modulations of the surface oxygen coverage induced by reactions of a target gas with ionosorbed oxygen species, successfully predicts that at elevated temperatures semiconducting oxides can be used as gas sensitive resistors to monitor, as impurities in air, any gases that can react in such a way as to alter the quantity of charge trapped at the surface. The latter results in variations in the Schottky barrier height and hence conductance response.

Such a mechanism certainly accounts for the well known lack of native specificity exhibited by metal oxide sensors. At elevated temperatures semiconducting oxides are sensitive to a wide range of gases, including CO, H\textsubscript{2}, NO\textsubscript{x}, SO\textsubscript{2}, hydrocarbons and organic vapor \cite{56,57}. In the course of a survey of the gas response characteristics of a wide range of different semiconducting oxides, reported by Moseley \textit{et al} \cite{51,56}, it was demonstrated that a general effect of minor concentrations of a reducing gas in air was to cause a resistance decrease for n-type materials and a resistance increase for p-type materials. The opposite responses were recorded for oxidizing gases present in small concentrations in air.

(ii) Effects of moisture.

Of a particular concern is the cross sensitivity of metal oxides to water vapor. If it is not contained in the ambient air, water is produced during decomposition of many reducing gases and therefore is the most common interference factor during the normal sensor operation. Most oxide surfaces react readily with water and become partially covered with molecular H\textsubscript{2}O or hydroxyl groups on exposure to air under ambient conditions \cite{58-60}. Adsorption of water onto semiconducting oxides surface modulates the grain boundary contact resistance and hence induces conductance variations. Most metal oxides are therefore sensitive to water vapor \cite{43,57}. Variations in relative humidity in ambient air can
be substantial. The cross sensitivity of metal oxide sensors to moisture results in a baseline resistance drift, confounding the effects of the desired gas.

For devices using tin dioxide, the effects of variation of relative humidity are a factor of major importance. In a similar fashion to reducing gases, water vapor is known to increase the conductance of SnO$_2$ sensors, and in fact effects of adsorption and desorption of water vapor dominate the resistivity behavior below 350°C [44,52,61].

The conductance response to water vapor is attributed to dissociation of chemisorbed molecular water to give OH$^-$ attached by its oxygen end to the lattice tin and H$^+$ bounded to lattice oxygen to form a second type of hydroxyl group [43,62]:

$$
\text{H}_2\text{O} + \text{Sn}_{\text{lat}} + \text{O}_{\text{lat}} \rightarrow (\text{HO-Sn}_{\text{lat}})^* + \text{O}_{\text{lat}}\text{H}^* + 2n'
$$

The presence of two types of OH groups on a SnO$_2$ surface was concluded from infrared studies [63]. Therefore, exposure of an SnO$_2$ surface to moisture results in transformation of the major surface species from adsorbed ionized oxygen to hydroxyl ions. The conductivity of tin dioxide is controlled by Schottky barriers at intergranular contacts, with the barrier height determined by the population of the surface states. The trap state represented by OH$^\text{ads}$ is supposed to lie higher in the band gap than that represented by O$^{2-}$, to account for the transformation of O$^{2-}$ to OH$^-$ causing an increase in conductivity [44,61]. A number of thermal desorption studies have been reported for hydroxylated SnO$_2$ surface [64, 65]. In general the surface hydroxyl groups are stable and do not completely desorb even at 600K. The interaction of water vapor with tin dioxide surface, therefore, causes an irreversible resistance decrease at temperatures below 350°C.
(iii) Operating temperature

It should be noted that the generally accepted gas response mechanism is also a model for surface catalyzed combustion of the gas. It has been stated that the low temperature limit for detection of a particular target gas corresponds to the temperature of an onset of combustion of the detected gas over the sensor surface [25,66]. The conductance response (S) to a combustible gas in air is usually defined as Δσ/σ₀ for an n-type response (conductance increase in the presence of a reducing gas in air), σ₀ being the electrical conductivity in air; and as ΔR/R₀, for a p-type response (conductance decrease in the presence of a reducing gas in air), R₀ being the electrical resistance in air.

Generally speaking, S goes through a maximum with an increase in operating temperature, resulting in a volcano-shaped S vs. T dependence. Such a behavior has been shown to be a direct correlation between catalytic and sensor properties and related to the rate of catalytic oxidation of the reducing gas [55,66,67]. That is, the rate is still insufficient in the ascending region of the volcano (lower temperature side), while it is too high in the descending region (high temperature side). The latter situation arises because the sensor element has a thickness for the gas molecules to diffuse in. When the rate is too high, the gas molecules are oxidized preferentially in the surface region of the element, failing to reach the inner region. The maximum response (Sₘ) and the temperature (Tₘ) at which the maximum is reached depend markedly on the sensor material and the target gas, so that a certain degree of selectivity can be obtained by operating temperature control [25,67]. Metal oxides tend to give higher Tₘ and modest values for Sₘ to many reducing gases, reflecting the moderate catalytic oxidation activities of the oxides [66].
(iv) Effect of catalysts.

Due to a strong correlation between the gas sensing mechanism and surface catalyzed oxidation, materials with catalytic properties are often added to semiconductor gas sensors as second-phase particles in order to encourage the key reactions to proceed at lower temperatures. Decoration of an oxide surface with noble metal particles results in acceleration of the surface catalyzed oxidation of the target gas over the sensor surface, which causes the maximum in the volcano plot of conductance response (S) vs. temperature to be shifted to lower values of $T_M$ [68,69].

For sensors fabricated in a form of finely porous sintered ceramics the gas penetrates the body by diffusion down the pores. The effect of catalytic surface additives depends strongly on the operation temperature, device geometry and microstructure. In particular, due to high catalytic activity of the metal additives, catalyzed combustion might reduce the concentration of the target gas essentially to zero in the sensor interior zone sampled by electrodes, hence removing the response at higher temperatures, as for example was reported for Pt/SnO$_2$ and Pd/SnO$_2$ systems [70]. The effect might manifest itself in apparent selectivity of the surface decorated device to a less reactive gas over the more reactive components. F. Menil et al [71] reported selectivity to CH$_4$ over ethanol of Pt modified porous SnO$_2$ thick film. The effect of Pt was to burn out a maximum ethanol hence removing the conductivity response of tin oxide to ethanol, but not to methane.

As well as lowering the operating temperature, decoration of the oxide surface with small noble metal particles like Pt [15,17,70], Pd [66,69,70], Ag [66,70] or Au [15,67] is known to modify the pattern of selectivity of conductance response to different gases and to promote the sensitivity. A reaction occurring on the catalyst will not necessarily affect the conductance of the supporting semiconductor. Modification of the gas sensing characteristics of surface decorated oxides, therefore, implies a synergistic interaction between metal additives and semiconducting oxide elements. The specific mode of interaction between metal additives and semiconducting oxide and therefore the mechanism whereby the catalyst modifies the response of semiconducting oxide depends on catalyst loading, its chemical form, distribution and particle size. The promoting effects of supported
noble metals can be divided into [72]chemical effects, mediated by promotion of catalytic activity of the oxide surface by metal additives; and electronic effects, where metal additives cause modification of surface states of the oxide modulating the intergranular contact potential and hence electrical behavior of the material.

In general it is found that the temperature of the maximum response, \( T_M \), in surface decorated oxides is parallel to the temperature at which the rate of catalytic oxidation of the target gas reaches a certain level [66,73,74]. In this case the effects due to catalytic metal additives can be generally classified as chemical sensitization, mediated by “spillover effects” reviewed in heterogeneous catalysis [75-80]. The supported metal particles are thought to provide the preferential adsorption sites for the reactive gas species to be activated and spill over to react with chemisorbed oxygen on the oxide at metal/oxide interface [79,80]. Results of Sn-119 Mossbauer spectroscopy studies were reported by Kulshreshtha and Sasikala [79] for Pd/SnO\(_2\) and Pt/SnO\(_2\) catalysts. Direct evidence in support of the spill over of H\(_2\) and CO from metal sites to SnO\(_2\) support was provided. They showed that treatment of the samples in H\(_2\) or CO flow resulted in the formation of Sn\(^{2+}\) species in all cases. The extent of Sn\(^{2+}\) formation was found to be dependent on the metal content. Spillover of H\(_2\) and possibly CO on Pt-SnO\(_2\) has also been suggested by Bond et al [80].

The model of gas detection in catalyst modified oxides developed by Kim and Kang [81] is based on the ability of the catalyst to dissociate molecular oxygen and to spill it over onto oxide at metal/oxide interface, increasing the oxide sorption capacity at the interface. Preferential adsorption of oxygen at the metal/oxide interface as ionized species was supposed to cause the formation of an extended dipole double layer at the interface. The gas-sensitive conductance response was then explained by modulation of the dipole double layer as a result of interaction of a reducing gas with ionosorbed oxygen species at the metal/oxide interface, hence the gas response mechanism was assigned to surface catalyzed combustion.
The effect of oxygen spillover was observed by Grass and Lintz [76,77], who studied adsorption of oxygen on Pt-SnO₂ catalyst. Independent variations in SnO₂ and Pt surface areas allowed them to demonstrate that oxygen adsorption sites were not equally distributed over the SnO₂ surface, but were preferentially located around Pt particles. They showed that Pt particles increased the sorption capacity of tin dioxide, as the oxygen adsorption increased more than linearly with Pt surface area at constant SnO₂ area. Boulahouache et al [78] showed, in agreement with Grass and Lintz [77], that the rate of CO oxidation increased with extension of the three phase boundary line gas-noble metal-oxide, signifying that catalytic CO oxidation involved preferentially oxygen species chemisorbed at the metal/oxide interface.

Unlike the chemical interaction between metal additives and semiconducting oxide support, which has been well investigated in the catalytic literature, the electronic promoting effects of the noble metals in gas sensing are less familiar. Such effects are believed to arise when the electronic properties of the surface catalytic additives dominate the support response mechanism. In some particular cases, gas sensitive electrical conductivity in surface decorated oxides has been induced at room temperature as a result of such electronic interactions [70,74,82,83].
1.3 Effects at room temperature in surface modified oxides

1.3.1 Phenomenon

The optimum use of precious metal additives was shown to induce a gas sensitive electrical conductivity in surface decorated oxides at room temperature [70,83]. Such effects were sensitive to preparation conditions and the base materials used.

Yamasoe et al [74] reported the effects of Pd, Pt and Ag additives (0.5wt%) on a gas sensing behavior of porous SnO\textsubscript{2} sinters. SnO\textsubscript{2} powder was prepared from metallic tin by dissolving it in hot nitric acid, precipitating and firing at 600\textdegree C. The powders were loaded with catalysts by impregnation of salt solutions, pelletized and further sintered at 600\textdegree C. The effect of catalytic metal additives was to increase the resistance of SnO\textsubscript{2} in air at room temperature. The magnitude of the resistance increase was dependent on the particular additive and the lowest value was shown for Pd/SnO\textsubscript{2} sample. The gas sensing behavior was also modified, but again the effect was different depending on the additive present. The Pt/SnO\textsubscript{2} system, in particular, was worth noting, as a maximum in conductance response of several orders of magnitude was actually recorded at room temperature for both CO and H\textsubscript{2}. On temperature increase a sharp drop in sensitivity was recorded. An interesting effect was also observed for the Ag/SnO\textsubscript{2} system, where the conductance was extremely sensitive indeed specifically to H\textsubscript{2} at room temperature, but showed no response to CO.

McAleer et al [83] reported a study on Pt, Pd and Ag modified SnO\textsubscript{2}. Tin dioxide was formed by decomposition of metastannic acid at 1000\textdegree C, followed by further sintering of the prepared pelletized sensors at 1000\textdegree C for 16h. Surface additives were applied by impregnation of the pelletized samples with an aqueous solution of metal salts. The impregnation conditions and low decomposition temperature resulted in all the additive being located at the gas/semiconductor interface in a very finely divided state in each case. SnO\textsubscript{2} surface modification with Pt and Pd resulted in a modified conductance response to CO and H\textsubscript{2}. Maximum response to both CO and H\textsubscript{2} was observed at room temperature, with a sharp loss in gas sensitivity with temperature increase. It was shown that the maximum gas sensitivity was actually observed below an onset of combustion. In fact, the onset of surface
combustion for Pt and Pd modified samples corresponded with the loss of gas-sensing response. The important aspect of this work was the catalyst modified conductance response to moisture at ambient temperature in Pt/SnO$_2$ and Pd/SnO$_2$ systems. Moisture is known to cause a large irreversible resistance decrease of SnO$_2$ at low temperatures [44, 46, 52]. The effect of surface modification with Pt and Pd was to completely remove the irreversible conductance behavior of SnO$_2$ in the presence of water and to diminish the actual value of the water induced response. It was taken that the surface modification with precious metal eliminated the effect on the conductivity of the transformation from adsorbed ionized oxygen to hydroxyl ions as the major surface species.

The work of Matsushima et al. [84] clearly demonstrated the strong dependence of the low temperature conductivity and gas sensitivity of Pd modified SnO$_2$ on Pd particle size and dispersion. The SnO$_2$ powder was prepared following the route of Yamasoe et al. [74], but Pd was applied in three different ways: by chemical fixation using a solution containing ([PdCl]$_4$) complex, through colloidal suspension with Pd particles 1-5nm, and by simple impregnation method. The resultant Pd loaded samples were calcined at 700$^\circ$C for 5h, and the surface state of Pd was identified as PdO in each case. In each case metal loading was about 0.2-0.3%, but it was shown that impregnation method resulted in far lower Pd dispersion compared to the colloidal and the fixation methods. The fixation method gave average Pd particle size (D) of 1.6nm with very narrow particle size distribution, followed by colloidal method with D=2nm and finally by impregnation method with D=3.8nm and with broad size distribution ranging up to 10nm. In each case Pd loaded samples showed an increase in the electrical resistance in air at room temperature, compared to pure SnO$_2$. The magnitude of the resistance increase, however, was shown to correlate with Pd particle size and dispersion, smallest effect being for the impregnated sample. The gas sensing behavior was also shown to be strongly dependent on the Pd dispersion. The impregnated sample showed the lowest conductance response to H$_2$, which was negligible at ambient temperature and increased with temperature increase, showing a maximum response at 200$^\circ$C. However, the two other samples prepared by fixation and colloidal methods, showed a maximum conductance response to H$_2$ at temperatures around ambient, with a sharp drop on temperature increase, to virtually zero above 250$^\circ$C.
Since the addition of catalyst gave rise to an increase in baseline resistance and moved the maximum response to the lowest temperature tested (that is to a temperature below the onset of combustion), it was suggested that the actual mechanism of the conductance response in those particular cases had been modified.

1.3.2 Model of room temperature response.

In general the conductance change of heated metal oxide sensors in response to a range of gases usually comes from the reaction of these gases with a single adsorbed species, which itself acts as an extrinsic surface acceptor state, controlling the charge carrier concentration. These common species are identified with ionosorbed oxygen. The surface noble metal additives are believed to modify the response mechanism, inducing the room temperature gas sensitivity. In particular it is believed that the supported metal particles themselves provide the surface trap states, controlling the conductivity, with the response originating from a specific interaction between target gas and metal particle, for which semiconducting oxide support serves as a transducer [83].

(i) Interaction of gases with catalytic metal surfaces.

Gas exposure changes the electrical and/or electronic state of a metal surface due to adsorption processes [41]. Gas adsorption can be crudely divided into two stages: a weak adsorption, called physisorption, due to dipole interactions, and a strong one called chemisorption, due to covalent bonding. As it was pointed out earlier, a parameter that is sensitive to physisorption as well as to chemisorption is the work function, defined as the energy difference between the vacuum, $E_{\text{vac}}$, and the Fermi $E_F$, level. Variation in the Fermi level, therefore, is reflected in the variation in the work function.
CO adsorption on noble metal surfaces is non-dissociative at room temperature [85-87].

The generally accepted model for the CO-metal bond is a combination of 5σ donation from the highest occupied CO orbital to the metal and metal to CO back-bonding through a CO 2π* orbital. The net result of the synergistic interaction is believed to be an electron transfer from the metal to the CO species, primarily owing to back bonding with 2π* [87]. CO is predominantly adsorbed on step sites in a linear form at small coverages on Pt [88] and Pd [89], since the binding energy of CO for those sites is 8-10 kcal/mol higher than that on terrace sites [88,89]. The total saturation coverage for Pt(111) was reported as 0.63 ML [90]. The crystallographic dependence for CO adsorption is quite strong. For CO adsorption on Pt (111) steps Collins et al. [91] reported slight variation in the work function ΔΦ = +0.05eV and Netzer et al. [90] reported no variation in the work function.

Oxygen interaction with the Pt(111) surface was studied by Gland et al. [92]. They demonstrated that adsorption of molecular oxygen on Pt predominated below 120K. The measured work function change was ΔΦ = +0.8eV, indicating electron transfer into the molecular oxygen overlayer. They showed that the primary bond between molecular oxygen and the platinum surface was formed by electron transfer from the platinum valence band into orbitals, derived from the π* orbitals of adsorbed oxygen molecules. Above 170K dissociation of adsorbed molecular oxygen occurred. Adsorbed atomic oxygen formed a (2X2)-O LEED pattern on both flat and stepped Pt(111) surfaces. The saturation coverage on Pt(111) was reported as 0.5ML (monolayer). Work function measurements were conducted by Netzer et al. [90] for a (2X2)-O covered Pt(111) surface. An increase in the work function by as much as ΔΦ = +0.55eV on atomic oxygen adsorption was reported.

Oscillatory reaction rate behavior of the CO oxidation over a Pt(110) surface under isothermal (200°C) low-pressure conditions was reported by Ertl et al. [93]. The oscillatory reaction rate was shown parallel variation in the work function ΔΦ, taken as proportional to the oxygen coverage. Yeates et al. [94] reported the study of the oscillatory reaction rate of CO₂ formation over Pt (111) and (110) single crystals surfaces at atmospheric pressure. They showed that oscillations in the rate of CO₂ productions were due to cyclic oxidation and reduction of the Pt surface. For low CO concentrations surface oxide formation was
favored at low temperatures. Pt oxidation, however, is known to be highly passivating [95] and is essentially limited to the surface layer of Pt atoms.

Electronic properties of metal surfaces are different from those in the bulk metal due to a reduction in the atomic coordination on the surface. The reduced coordination number for the surface atoms leads to narrower, more atomiclike \( d \) bands with reduced \( s-d \) hybridization and an overall average configuration intermediate between those of the free and bulk atoms [96]. Hence, the electron binding energies of atoms in the surface of a metal should be intermediate between those in the bulk and those in the free atom. Photoemission is an especially useful probe of electronic structure and has been applied by a number of groups to study the differences between the surface and bulk metal properties [87,96,97]. A surface atom core-level shift towards lower binding energy is generally found in noble metals along with a narrowed surface density of states, since \( d \) orbitals are more localized. In the case of Pd and Pt the surface core level shift was measured to be -0.25eV [96] and -0.36eV [97] respectively.

The potential at the surface atom is altered by charge donation to or from the adsorbate and adsorption-induced surface core-level shifts have been reported for atomic oxygen, hydrogen and CO adsorption on Pt (110) [97]. The surface Pt 4f core level peak was found to shift to higher binding energies in all three cases. A binding energy shift of 1.26eV was reported following CO adsorption, 1.01eV shift for atomic oxygen adsorption, and 0.18eV shift for \( \text{H}_2 \) adsorption. A surface core-level shift of 1.1eV towards higher binding energies was reported for CO adsorption onto \( \text{Pt}_{0.98}\text{Cu}_{0.02}(110) \) by Shek et al [87]. The shifts cannot be explained by a simple charge transfer model, since adsorbates such as CO and \( \text{H}_2 \) are much less electronegative than atomic oxygen. Apai et al [98] suggested that the potential at the surface atom is largely dependent on the charge redistribution over the \( d \) orbitals, regardless of the net charge transfer. The large surface core-level shift induced by CO compared to that due to \( \text{H}_2 \) adsorption was explained by the significant \( d \) bonding character of the former. UPS studies on CO adsorption on various Pt single crystal and polycrystalline surfaces were reported by Collins et al [91], who showed a CO-induced decrease in emission in the Pt valence band spectra just below the Fermi level in each case. The reduction of intensity at the Fermi level was attributed to screening of the signal from
the underlying metal and to charge donation from the metal $d$-band near the Fermi level into the $2\pi^*$ level. The lack of changes reported in the bulk core level [87] following gas adsorption indicated that the adsorbate-metal bonding is localized within the topmost surface layer.

Electronic properties of supported metal catalysts with the particle size reduced to the point where most of the atoms are on the surface should be related to those of the atoms within a surface plane of the bulk solid. Small metal clusters are also characterized by narrower, more atomic-like $d$ bands due to increased localization [96,99]. A number of photoemission studies on small metal clusters have reported band-narrowing of the valence band spectra with decreasing cluster size [99-101]. By varying the size of the cluster, the transition from an atomic (finite) to metallic (infinite) system can in principle be observed. Theoretical calculations indicate that more than one hundred atoms, corresponding to particle dimensions of 2.0-3.0 nm, are required before bulk electronic structure is observed [102]. Interestingly this is also the size range in which changes in catalytic activity have been observed with supported metal catalysts.

Wertheim et al [99] showed valence band narrowing with decreasing cluster size for Ag and Pd clusters supported on amorphous carbon. They pointed out that the valence region provides direct information about the cluster-size-related changes of the electronic structure, since the bandwidth is roughly proportional to the square root of the coordination number. The size of the cluster too small to be considered metallic was estimated to be 1nm for Ag and 1.2nm for Pd.

Altman et al [102] reported XPS and UPS studies of Pt particles, supported on $\text{Al}_2\text{O}_3$. For particle size below 2.5nm they reported Fermi edge broadening and shift of about 1.0eV below that of the bulk Pt. They concluded that below 2.5nm in size Pt particles do not exhibit the electronic structure of the bulk metal. However, Altman et al [102] demonstrated that no changes were observed in CO induced features in the Pt valence band UPS spectra as Pt particle size was decreased below 2.5nm. In each case a decrease in the emission just below the Fermi level, characteristic of the $\pi$ back-bonding on CO-Pt bond
formation, was registered. They concluded therefore, that the bonding was very localized between the CO molecule and neighboring Pt atom and the electronic structure of the particle as a whole did not influence the nature of CO adsorption. This was also confirmed by the CO TPD studies in their later work [103]. They showed that the same CO desorption states were observed on Pt particles supported on Al₂O₃ as were observed on a Pt single crystal stepped surface. The local character of Pt-CO chemisorption bond was also confirmed by Roszak et al [104].

McCabe et al [95] studied by temperature programmed desorption the oxidation of Pt supported on SiO₂. The fraction of Pt that was oxidized at 300°C was shown to decrease with increasing particle size, ranging from essentially complete oxidation for particles of less than 1.5nm to less than 10% for particles over 4.0nm. They showed that Pt oxidation was highly passivating; the oxide film thickness was less than or equal to one monolayer equivalent of Pt atoms, regardless of O₂ pressure, temperature (300 - 500°C) or length of exposure. Since only exposed Pt atoms were oxidized, complete oxidation was limited to a particle size where most of the atoms were on the surface, corresponding to the transition to particles too small to be considered metallic.

Gaidi et al [105] reported the in-situ EXAFS analysis of the variations induced by oxygen and CO adsorption in the local environment of Pt particles supported SnO₂. The correlation between the X-ray absorption at the L₃ edge and the occupation of the metal 5d band was used to determine the variations in the Pt electronic state: the greater the white line intensity, the less the occupation of the d band and the more oxidized the platinum. They demonstrated oxidation of supported Pt to PtO₂ in air and reduction when the atmosphere changed to N₂+900 ppm CO, in the temperature range 50 - 350°C. Important particle size effects were demonstrated. The change in the white line was particularly pronounced for the finest (3nm) particles and was very weak for larger (5nm) particles. They proposed that the finest particles had the highest oxidation state, since all the bulk of the supported Pt was oxidized, whereas for the big particles only the surface was oxidized and the metallic phase widely prevailed.
Oscillations of the reaction rate of catalytic oxidation of CO over a highly dispersed Pd catalyst in a zeolite matrix were studied by Jaeger et al [106]. The complete oxidation of 2 - 2.5 nm Pd crystallites was demonstrated under 5 vol% CO in synthetic air at 180°C, causing a drop in the CO oxidation rate. This was followed by reduction of the oxidized PdO by CO with an increase in the reaction rate. The oscillations were stronger for finer Pd particles and it was suggested that the small particles are much more easily oxidized and reduced.

(ii) Metal-semiconductor interaction.

When a contact is made between a semiconductor and a metal, the free energy of electrons will, in general, not be identical in the two partners in insulation and must be equalized when the contact is made. An idealized example of a contact between a noble metal of high work function, $\Phi_m$, in contact with an n-type semiconducting oxide of lower electron affinity, $\chi_{sc}$ in given in Fig 1.8 [107].

Figure 1.8 The energy band diagram through the metal-semiconductor contact - the Schottky contact, for the case where the work function is greater than the electron affinity [107].
To satisfy the requirement of electronic equilibrium requires a flow of the charge from semiconductor to the metal, which gives rise to a region of charge depletion in the semiconductor and a potential barrier at the solid interface. The height of the potential barrier, \( \Phi_{MS} \), on an n-type semiconductor, known as a Schottky barrier, is given by [107]:

\[
\Phi_{MS} = \Phi_M - \chi_{SC} \quad (1.13)
\]

And the barrier from the semiconductor to the metal, defined as a band bending in the semiconductor or the "built in potential" [107]:

\[
-e\Delta\phi_s = \Phi_M - \Phi_{SC} \quad (1.14)
\]

The above corresponds to an idealized contact, since there will normally be some interface states between the metal and the semiconductor which may accept or donate charge, altering the characteristics of the junction. These interface states may be crystalline defects or impurity species.

The study of variations in electronic structure of TiO\(_2\) and SnO\(_2\) in contact with Pt or Pd surface dopants was reported by Schierbaum et al [108]. SnO\(_2\)(110) and TiO\(_2\)(110) single crystals were used and Pt or Pd were evaporated in submono- and multilayer range. The recorded current-voltage curves for SnO\(_2\)/Pd (0.7ML) and TiO\(_2\)/Pt (0.2ML) showed nonlinear Schottky diode behavior, signifying that the overall conductivity was determined by charge transfer across Schottky metal-semiconductor contacts, with strongly depleted concentration of free electrons. For SnO\(_2\)/Pd with 0.7ML Pd coverage a band bending \(-eV_0 = 1.22 \text{ eV}\) was reported with respect to a flat band situation of the stoichiometric surface.
(iii) Room temperature response

The implication of such electronic interaction between metal particles and semiconductor for room temperature gas sensitivity of surface decorated SnO₂ is as follows. It is generally accepted that the conductivity of porous sintered SnO₂ ceramics in air is controlled by a Schottky barrier mechanism operating at intergranular contacts, with the barrier height being dependent on the occupancy of the surface states associated with ionosorbed oxygen. For surface decorated SnO₂ the surface states would be modified by metal additives. Because of the high work function of Pt (5.4eV [83]) and Pd (4.8 [82]), small particles of these metals would act as 'surface states' lying lower in energy than those associated with oxygen species. Therefore, the Schottky barrier height and the space charge region depth for noble metal modified intergranular contacts would be expected to increase due to electron transfer between the metal derived surface states and the bulk. For the electrical behavior of the device to be modified, metal particles must be uniformly distributed over the oxide surface, so that the depletion layers around each metal particles overlap Fig 1.9.

Figure 1.9 (a) Schematic diagram of the possible effect of small precious-metal particles on the depletion layer width and intergranular barrier height. (b) Electron energy profile controlled by surface oxygen species only (—). Electron energy profile controlled by precious-metal particles (___). Extracted from McAleer et al.[83]
The electrical conductivity of the material in this case would be controlled by a Schottky barrier mechanism, associated with the contact potential formed at the metal/oxide interface. The barrier height would now be determined by the population of metal derived surface states. Hence a resistance increase would be expected for surface decorated oxides, compared to the unmodified case. A resistance increase was indeed recorded at room temperature in air for sintered SnO$_2$ ceramics, decorated with Pt [109], Pd [74,82,84] and Ag [74,82].

Shimizu et al [110] studied porous sintered SnO$_2$ devices loaded with Pt, Pd, In or Rh(0.1-1 wt%). They reported a significant increase in a breakdown voltage for each device in air, compared to pure SnO$_2$. The magnitude of the increase was dependent on the noble metal, and at 0.1wt% loading was shown to correlate well with the electron work function of the metal additive. The highest breakdown voltage in air was recorded for the Pt loaded sample and the work function of Pt was the highest of the noble metals tested. At loadings exceeding 0.1wt% the correlation became obscure and a slight decrease in a breakdown voltage was observed for each device. This was explained by non-uniform dispersion of the metal particles due to agglomeration with increased coverage.

To explain the effect of room temperature conductance response to CO and H$_2$ in porous sintered SnO$_2$ ceramics decorated with small Pt or Pd particles McAleer et al [83] proposed that, in the case when the electronic interaction between the metal and the oxide dominated the electrical behavior of the material, the conductivity was controlled by the surface state of the metal additive rather than being determined by the surface state of the oxide. A change in the electronic state of the additives, if it happened on contact with reducing gases, would cause a change in surface conductivity of the oxide which in this case serves as a transducer. In other words the gas sensing behavior of surface decorated oxides will be modified if reactions occurring on the catalyst affect the transduction properties of the supporting oxide. McAleer et al [83] postulated that the room temperature CO and H$_2$ conductance response was due to gas chemisorption on to precious metal. Adsorption of CO and H$_2$ on Pt results in partial charge transfer [97]. For small enough Pt particles the charge transfer could be large enough to perturb the total free-electron charge within the particle. As a result the electron exchange between the metal additives and the oxide
support would be altered, causing variations in the degree of band bending and hence conductivity. It was estimated that such an effect was limited to Pt particle size of about 1nm. Hence another important role of SnO\(_2\) support in this case is to stabilize ultrasmall metal particles.

In later work Henshaw et al [109] demonstrated that the proposed model was indeed correct, in that the effect of room temperature CO response was very sensitive to the particle size of the Pt crystallites and was lost when the latter exceeded 8nm. They further refined the model by noting that the room temperature CO response was recorded only in oxygen ambient. As noted in section 1.3 the change in the workfunction due to O\(_{\text{ads}}\) on Pt (\(\Delta \Phi = +0.55\)eV) is greater than for CO\(_{\text{ads}}\) on Pt (\(\Delta \Phi = +0.05\)eV). It was therefore proposed that the conductance response was due to CO adsorption on to a oxygen precovered Pt surface and displacement of chemisorbed oxygen, causing a change in the Pt work function and hence a change in the band bending in the oxide support. For uniformly distributed Pt particles of 1nm in size the proposed model correlated well with the observed power law dependence of CO response on gas concentration.

Yamasoe et al [74] and later Matsushima et al [82] proposed that the surface conductivity of Pd or Ag modified porous SnO\(_2\) was directly connected with the redox state of the metal additives. In air both Pd and Ag particles, or at least their surface region, oxidize to PdO and Ag\(_2\)O. On the metal/oxide interface each oxidized Pd particle forms a redox couple Pd\(^{2+}\)/Pd, the electronic potential of which is located 5.5eV below the vacuum level, whereas electron affinity of SnO\(_2\) is 4.49eV. Pinning of the Fermi level of the oxide at the Pd\(^{2+}\)/Pd redox potential would then occur with corresponding band bending of 0.6eV. On exposure to hydrogen at room temperature reduction of Pd\(^{2+}\) to Pd\(^0\) takes place, causing an upward shift of the SnO\(_2\) Fermi level, to become pinned at the level of the work function of Pd\(^0\) (4.8eV). The proposed model was based on the experimental results where oxidation/reduction of both Pd and Ag at room temperature on air/hydrogen cycles was confirmed by XPS.
1.4 The aims and objectives of this work.

It is believed that the modified gas sensitive behavior of surface decorated oxides at room temperature is based on a novel conductance response mechanism whereby the supported metal particles control the transduction properties of the semiconducting oxide while themselves acting as the receptor of a gas sensing action. To date the phenomenon has been limited to supported noble metal catalysts as Ag, Pt and Pd and a very few gases, in fact only CO and H$_2$. The general idea, however, that surfaces could be modified so as to endow them with properties that they lacked in their pristine state constitutes the main concept of this work.

As it was pointed out earlier most oxides react readily with water and the surfaces of inorganic oxides are usually covered by monolayer-hydroxyl groups in ambient air [59,111,112]. The surface hydroxyl groups are important functional groups, which can interact with organometallic transition metal complexes. Hence catalysts surface modification can be achieved through supporting organometallic precursors on inorganic oxides surfaces [112, 113]. By extending the concept of what has become known as interfacial coordination chemistry [114], surface organometallic chemistry [113,115], and shape selective catalysis, the surface grafting of reactive centers onto ceramic oxides has recently been developed as a route to active selective catalysis [116-118].

For example it has been shown how the mesoporous silica may be functionalized with organometallic precursors and converted to well defined, single-site heterogeneous catalysts. In particular Maschmeyer et al [119] reported engineering of supported well defined, isolated Ti$^{IV}$ active centers for the catalytic epoxidation of a range of alkenes via direct grafting of titanocene dichloride onto the inner walls of a high area silica support. Isolated vanadyl active sites in silica-based catalysts for selective oxidation of hydrocarbons obtained by anchoring of vanadocene dichloride onto inner surfaces of silica were reported by Oldroyd et al [116].
The synthesis of the reactive Rh dimer complex, bound to an SiO₂ surface through Rh-O(surface) bonds was described by Asakura et al [120], based on interaction of a Rh dimeric organometallic precursor with OH groups of SiO₂. The attached Rh dimer site was remarkably active and highly selective for ethene hydroformylation. Asakura et al [121,122] have also reported the formation of polynuclear (n=1-6) surface bound unsaturated Ru clusters, highly active for CO hydrogenation through anchoring Ru carbonyl complex onto various inorganic oxide supports.

The work reported in this thesis is concerned with the possibility that reactive centers grafted onto a semiconducting oxide via organometallic precursors could modify the electrical conductivity of the oxide, by acting as surface trap states. The variation of the electrical conductivity would then signal changes in the chemical state of the grafted center, such as might for example be caused by adsorption of a gas molecule onto this site.

The detailed characterization of the local environment of the attached mononuclear or polynuclear active sites has been performed with the aid of synchrotron radiation, by X-ray absorption near-edge structure and extended X-ray absorption fine structure. These coupled with appropriate catalytic reaction cells have allowed monitoring of the state of the catalyst from the initial state of synthesis through to the active state of the catalyst during the operation and at the final state [116,117].

In this work we propose the application of surface grafting techniques to provide particular reactive centers equivalent to surface electronic states positioned within the band gap of the oxide which can communicate electronically with the oxide so that the electrical conductivity of the oxide can conceivably be used to monitor the chemical state of the grafted species. Appropriate choice of the reactive center could then lead to interesting new types of gas detectors tailored for a particular application or an interesting complementary way of following changes in a chemical state of an active catalyst during a reaction.
1.5 Outline of this thesis.

The present work derives its motivation and approach from the reported modified gas sensing behavior of finely porous sintered SnO$_2$ decorated with sufficiently small particles of Pt, equivalent to surface trap states controlling the conductivity. In the first part of this work which is outlined in Chapter III, the room temperature conductance response mechanism in this system is examined in detail.

Although supported platinum has been widely used as a promoter of the gas sensing characteristics little is known about the role of oxidized platinum surface species in the gas sensing action. Henshaw, Ridley and Williams [109] reported the study of the effects of Pt particle size, dispersion and the surface state of the Pt on the room temperature gas sensing behavior of Pt decorated SnO$_2$. In the final stage of the sensor preparation, the decomposition temperature of the precursor Pt complex was varied between 300 and 800°C. In this way variation in Pt particle size and chemical state was obtained simultaneously, the latter being determined by XPS. The effect of Pt surface additives was to increase the base line resistance of SnO$_2$ in air at room temperature. Pt was shown to introduce states in the band gap of SnO$_2$ above the valence band edge and induce an increase in the band bending. Hence an electronic interaction between Pt additives and SnO$_2$ support was proposed. The authors showed that CO sensitivity at room temperature decreased with an increase in particle size of the Pt crystallites and the effect was lost when the latter exceeded 8nm. Increase in the Pt particle size with decomposition temperature coincided with variation in the Pt speciation. In the active sensor the chemical state of the surface Pt was shown to be a mixture of Pt$^0$ and Pt(OH)$_2$. The relative amounts of both species varied with decomposition temperature, as did the Pt particle size. In the developed model the variations in the room temperature CO sensitivity of the electrical conductivity was assigned to the increase in the Pt particle size. The effect of variation in the Pt speciation, therefore, remained unclear. Catalyzed combustion was recorded for CO over the active sensor. Since both Pt$^0$ and Pt(OH)$_2$ were found on the surface of the active sensor both species were proposed to induce the combustion of CO at room temperature.
In the work reported in this thesis we obtain variation in the Pt speciation independently of the particle size and show the sensitivity of the electrical conductivity to the surface state of Pt. We demonstrate that the materials which exhibit only Pt\(^0\) species catalyze CO oxidation at room temperature, but show no CO sensitivity of the electrical conductivity at room temperature. We show that the room temperature CO response is due to CO adsorption onto specific Pt(II) surface sites.

The second part of this work, described in Chapter IV, is concerned with surface modification of SnO\(_2\) via surface-grafting of Ru active centers. We give a method for surface grafting of Ru onto SnO\(_2\), characterize the grafted centers, demonstrate electrical conductivity changes at room temperature caused by gas adsorption and correlate this with changes in the chemical state of the surface grafted Ru determined by X-ray photoelectron spectroscopy.

The structure and reactivity for CO hydrogenation of the Ru centers derived from Ru\(_3\)(CO)\(_{12}\) supported on various inorganic oxides was described by Asakura et al [122]. They showed that in the case of Ru/SiO\(_2\) following decomposition in H\(_2\) at 500\(^\circ\)C small supported metallic Ru particles were formed and no apparent Ru - O(surface) bonding was found. An average particle size was determined as 1nm with nuclearity of 12. In the case of Al\(_2\)O\(_3\)/Ru, however, supported Ru clusters were formed which were characterized by Ru-O-Al bonding and low coordination number of 3.1. Hence Ru\(_6\)-framework surface bound clusters were deduced. They showed that chemical interaction between metal species and support through the Ru-O-support bonding was an essential factor in the activity and selectivity of Ru catalysts and proposed that such interactions controlled local structure and electronic states of metal sites. The Ru-O-support interaction was taken to control the oxidation state of Ru atoms and it was pointed out that all Ru atoms in small clusters constitute highly unsaturated Ru sites. The preferential formation of higher hydrocarbons (>C\(_3\)) over the sample was attributed to the fact that CO can multiply adsorb on such unsaturated Ru sites.
Resent work by Chaudhary et al [123] described the performance of Ru modified tin dioxide sensors. The surface of tin dioxide was functionalized with ruthenium oxide via immersion of sintered SnO₂ pellets in a dilute solution of ruthenium chloride in isopropanol/water, drying and sintering for 2 hours at 400-650°C in air. On the basis of TGA analysis they claimed formation of strongly anchored Ru species on the surface of tin dioxide. The formation of well dispersed particles of RuO₂ was, claimed on the basis of SEM images and the oxidation state of Ru was identified by XPS, corresponding to RuO₂ with some Ru metal. The gas sensitivity of the samples to LPG (liquid petroleum gas), H₂, NH₃, H₂S and CO was examined at 300°C. The surface-ruthenated SnO₂ showed high sensitivity and selectivity to LPG at this temperature. RuO₂ on the surface was taken to act as a catalyst to enhance the oxidation rate of a combustible gas.

Matsushima et al [84] described the use of the fixation method to achieve highly dispersed nanometer Pd particles on SnO₂. The Pd chloro-complex [PdCl₄]²⁻ (prepared by dissolving PdCl₂ and NH₄Cl at 1:2 in water) was anchored on the surface of SnO₂ via reaction with the surface hydroxyl groups:

\[ [\text{PdCl}_4]^{2-} + 2\text{OH}^- \xrightarrow{\text{2NH}_4^+} \begin{array}{c} \text{Pd} \\
\text{Cl} \\
\text{Cl} \\
\text{O} \\
\text{O}
\end{array} \quad (2\text{NH}_4^+) + 2\text{HCl} \]

The fixed Pd species were subsequently converted to metallic Pd by heating at 300°C in hydrogen. Final pelletized samples were calcined at 600°C for 5h to convert supported Pd to PdO. The mean particle size, identified by TEM was found to be 2nm with a very narrow size distribution. Sensors showed high sensitivity to hydrogen with maximum at 100°C. An increase in the base line resistance was also recorded for Pd loaded samples. An electronic interaction between Pd and SnO₂ support was proposed and the gas sensitivity at 100°C was assigned to variations in the oxidation state of the supported Pd caused by interaction with the target gas.
Attached metal centers prepared by using the reaction between an organometallic complex and the support surface, often exhibit specific reactivities different from those of the corresponding supported metallic particles or oxides [124]. In this work we have used a monomeric Ru aryl precursor in acetone solution to functionalize the SnO₂ surface. We show that as a result of decomposition of the SnO₂-anchored Ru aryl complex in H₂ at 300°C surface bound unsaturated Ru clusters form. Grafting of unsaturated Ru clusters onto SnO₂ induced room temperature gas sensitivity of electrical conductivity. We also show that on formation of supported RuO₂ particles the effect is lost.

To complement the study of the gas sensing behavior of surface-ruthenated SnO₂, molecular cluster modeling, based on density functional theory (DFT) [125,126], was performed. This is outlined in Chapter V of this thesis. Trends in the behavior of molecular clusters, chosen to model the Ru modified SnO₂ (110) surface, are employed to shed some light on the origin of the conductance response in the Ru/SnO₂ system. In the simulations we did not attempt to calculate the actual electronic structure of SnO₂, but rather to probe trends in electrical behavior of the material induced by Ru surface grafting.

Over the last four years first principles quantum techniques based on density functional theory have been applied to solid-state problems for oxides and have made important contributions to understanding of oxide surfaces including MoO₃ [127,128], V₂O₅ [127,129], TiO₂ [130,131] and SnO₂ [131,132]. The approach is known to give accurate results for the energetics of lattice defects, surfaces and molecular adsorption [126,131]. Application of cluster model studies based on DFT to modeling of the surface defect sites [127-129] and bonding of molecules on to surface sites [129,133,134] has been reported. The study of electronic structure and bonding of non-stoichiometric lithium oxide clusters LiₙO₂ (n ≤ 10) by means of DFT molecular cluster modeling was reported by Finocchi et al [135]. DFT is a theory of the ground state and is designed to give accurate results for the valence electron distribution [125]. On the other hand it is known that DFT generally underestimates band gaps, as it is not designed to describe the excited-state properties [136]. However, as was pointed out by Finocchi et al. [135] it gives information on
the nature of the conduction states and on the overall stability of the cluster models. In this work the stoichiometric hydroxylated SnO$_2$(110) surface was modeled by molecular clusters of increasing size, Sn$_n$O$_m$H$_x$, and the variations in the electronic structure induced by the attached Ru were ascertained qualitatively by means of density functional methods. Finally the problem of adsorption of gaseous molecules onto attached Ru has been addressed.

In the final part of this work, outlined in Chapter VI, we set about to test the generality of the effect of modified gas sensing behavior in semiconducting oxides induced by surface modification. The argument developed in this work suggests that modification of an oxide surface with reactive species, alternative to electronic trap states positioned in the gap, induce the modified gas sensitivity of electrical conductivity. It then follows that such effect would be observed for any alternative semiconducting oxide, providing the electronic properties of the supported species exercise dominating control over the charge carrier density.

We report the preliminary studies on the gas sensing behavior of platinum decorated TiO$_2$-10%Nb, BaSn$_{0.97}$Sb$_{0.03}$O$_2$ and BaFeO$_{3-x}$. We demonstrate that in the case of TiO$_2$-10%Nb and BaSn$_{0.97}$Sb$_{0.03}$O$_2$ the effect of surface decoration with Pt was to induce the room temperature sensitivity of the electrical conductivity; we also show that BaFeO$_{3-x}$ does not show the effect. The differences in the behavior are explained on the basis of the differences in the XP valence band spectra of the three oxides.

We also show preliminary results of the effect of surface grafting of Ti onto SnO$_2$-0.2%Sb and TiO$_2$-10%Nb on gas sensing characteristics of the materials. Ti grafted samples, produced in this work show modified gas sensitivity of the electrical conductivity specific to each system.
The recent work by Maschmeyer et al.\cite{119} describes how to synthesize well defined, isolated Ti\textsuperscript{VI} active centers supported on mesoporous silica. The process entailed diffusing titanocene dichloride Ti(η\textsubscript{5}-C\textsubscript{5}H\textsubscript{5})\textsubscript{2}Cl\textsubscript{2} onto the interior surface of a crystalline mesoporous silica, suspended in chloroform, and subsequent anchoring of the compound onto the walls of the silica support via surface silanols, thereby producing a supported half-sandwich Ti(η\textsubscript{5}-C\textsubscript{5}H\textsubscript{5}) species. They showed by EXAFS that calcination in oxygen converted the grafted moiety into a four-coordinated site that functioned as the active catalyst center. In this work the developed route was adopted with some modifications. In particular the route involved using anhydrous acetone as a solvent, instead of chloroform. Residual chloride is known to affect both the microstructure and electronic properties of semiconducting oxide sensors \cite{137}. For example, it is known that the use of H\textsubscript{2}PtCl\textsubscript{6} as a Pt precursor suffers from the poisoning effects of the residual Cl\textsuperscript{-} left after decomposition \cite{138}.
Chapter 2. Experimental.

In this chapter the common preparations and the general characterization techniques are described. The particulars specific to each chapter are given therein.

2.1 Preparation

The SnO$_2$ used throughout this study was prepared by calcining metastannic acid (KEELING & WALKER) at 900°C for 3 hours in air. The material was then doped with 0.2 at% of antimony to increase the electrical conductivity to a range where changes would be easily measurable at room temperature: if the dopant level is too low, then resistances are too high for convenient measurement; if too high then the conductivity is so high that changes in surface trap states concentration have negligible effect. The correct stoichiometric amounts of SnO$_2$ and Sb$_2$O$_3$ (Aldrich, 99.995% pure) were mixed in a ball mill with acetone and ceramic beads for 24 hours. The mixtures were then evaporated and fired at 1000°C for 12 hours in air.

2.2 Materials characterization.

2.2.1 UV-Visible spectroscopy.

UV-visible absorption spectra were recorded on a SHIMADZU UV-160 spectrometer, operating within 200 - 1100nm wavelength range and 0 - 2.5Å absorbance range. A liquid sample cell of 1cm cross section was used and pure acetone was taken as a standard.
2.2.2 Resistivity measurements

The resistivity was measured in the apparatus, shown in Fig 2.1, using a Wayne Kerr automatic precision bridge. Powdered samples (1) were placed between gold electrodes (2) in the PVC pellet press (3) and a constant force of 300 kg was applied to each sample during the measurements.

Figure 2.1 Apparatus for resistivity measurements under a constant force applied to the samples.

2.2.3 X-ray photo electron spectroscopy

Surface analysis was carried out by x-ray photoelectron spectroscopy on Fisons Instruments Escalab 220i-XL. Monochromated Al-Kα X-rays were used with a 300μm spot size, and the sample pressure was less than 10⁻⁹ Torr. The analyzer pass energy was 20eV and spectra were acquired with 0.1 eV steps. When appropriate sample charging was controlled with a 3eV electron flood gun. Spectrum quantification and curve fitting was carried out using Shirley/Linear background and sensitivity factors obtained from Wagner et al. [139].
2.2.4 Gas sensitivity measurements.

The electrical behavior of the samples under controlled gaseous atmosphere, humidity and temperature was monitored using a 3-pellet test rig Fig.(2.2). The pellets were sandwiched between gold electrodes in a ceramic tube holder. Each pellet's electrodes were separated from those of the neighboring pellets by alumina spacers. The ceramic holder was inserted into a quartz tube through which the gases were passed. This was heated inside a tube furnace. Silica rod (S) provides pressure for contacts.

Figure 2.2 Schematic plan of a three pellet RIG for conductance response measurements.
Fig. 2.3 shows the experimental set up. Resistance measurements in the test rig were made every 60 seconds, using a KEITHLEY autoranging multimeter. Mass-flow controllers (Tylan) were used to control the gas flow and concentration through the quartz tube. To allow temperature control and complex gas concentration variations to be performed during the experiments, mass flow controllers, the furnace and the resistance measurements were computer controlled.

Figure 2.3 Schematic diagram of the experimental set up for the gas sensing characteristics measurements.
The gas response of the n-type sensors was defined as:

\[ S = \frac{(\sigma_g - \sigma_0)}{\sigma_0} = \frac{(R_{air} - R_{gas})}{R_{gas}} \] (2.1)

where \( \sigma \) denotes conductivity (\( \sigma_0 \) in air/nitrogen) and \( R \) the measured resistance. The power law dependence of the resistance response on gas concentration was assumed to be of the form [55]:

\[ \sigma = \sigma_0(1 + \kappa P_{CO}^\beta) \] (2.2)

where \( \kappa \) is the sensitivity and \( \beta \) is the response exponent. Gas sensitivity, \( \kappa \) was calculated from the intercept of the double logarithmic plot \( \log(\sigma_g - \sigma_0)/\sigma_0 \) vs \( \log P_{CO} \); and the response exponent, \( \beta \) from the gradient of the log-log plot.

2.2.5 Temperature Programmed Decomposition (TPDE).

Temperature programmed decomposition studies were performed in a UHV chamber, fitted with a Fisons Instruments quadrupole mass spectrometer. The base pressure was better then \( 10^{-8} \) torr. Powdered samples "as prepared" (0.1g) were placed in a quartz tube with an id of 2mm, around which a tungsten heater filament was fixed. The temperature of the sample was monitored directly using a Pt/Pt-Rh thermocouple, positioned half way into the quartz tube. A linear temperature ramp was achieved using a computer controlled power supply, applied to the heater element.
2.2.6 Temperature Programmed Desorption (TPD).

(i) UHV experiment

UHV TPD studies were performed using the same equipment and techniques as for TPDE. Prior to TPD studies samples were decomposed in vacuum and cooled down; their surface was probed at room temperature. For TPD of CO, pure carbon monoxide, supplied by BOC, was used without further purification. TPD of NO was performed using nitric oxide supplied by BOC without further purification. To study preoxidized surfaces oxygen (BOC) was used. Gases were applied using a stainless steel UHV leak valve.

SnO₂-0.2% Sb was used as a blank. The sample was heated to 400°C in vacuum and cooled down to room temperature. TPD of CO was used to probe the clean SnO₂-0.2%Sb surface, for which the sample was exposed to excess CO (8x10⁻⁶ torr for 5min), followed by evacuation to a base pressure of <10⁻⁸ torr. The temperature was ramped at 30°C/min from 25°C to 400°C. TPD spectra were acquired every 3 s for mass 28 (CO⁺) and 44 (CO₂⁻). Fig 2.4 shows the time profiles of mass 28 and 44 for the mass spectrometer signal.

![Figure 2.4 Temperature programmed desorption spectra of CO and CO₂ obtained after exposure of the reduced SnO₂-0.2%Sb to excess CO (8x10⁻⁶ torr for 5min) at room temperature. Heating rate 30°C min⁻¹.](image-url)
To study the oxygen precovered SnO$_2$-0.2%Sb surface the sample was exposed to excess oxygen (8x10$^{-6}$ torr for 5 min), followed by excess CO (8x10$^{-6}$ torr for 5 min) at room temperature. After evacuation to a base pressure of <10$^{-8}$ torr the temperature was ramped at 30$^\circ$/min to 400$^\circ$C. Fig 2.5 shows the mass 28 and 44 evolution signals, recorded mass spectrometrically.

![Temperature programmed desorption spectra of CO and CO$_2$ obtained after exposure of the reduced SnO$_2$-0.2%Sb to excess O$_2$ (8x10$^{-4}$ torr for 5 min), following by excess CO (8x10$^{-4}$ torr for 5 min) at room temperature. Heating rate 30$^\circ$/min$^{-1}$.](image)

(ii) Ambient pressure measurements.

TPD studies at ambient pressure were performed in a closed circulating system with a quartz reactor tube with id of 9mm and a quartz frit upon which 0.5g of the powdered sample was placed. Helium was used as a carrier gas, which was supplied to the reactor through mass-flow controllers (Tylan) at 100 cm$^3$ min$^{-1}$. The reactor tube was mounted vertically inside a tube furnace (Carbolite MTF 9/15), which could be programmed for the required linear ramp. The temperature of the sample was monitored directly with Pt/Pt-Rh thermocouple. The exit gas stream was continuously sampled using a stainless steel leak valve into a Fisons Instruments quadrupole mass spectrometer.
2.2.7 Combustion measurements.

Catalytic CO oxidation measurements were performed in a flow experiment using the same equipment and techniques as for ambient pressure TPD. CO was used in a 21%O₂ - He mix to remove the mass 28 interference by dinitrogen. Required concentration of CO in O₂-He mixture was obtained by dilution of pure carbon monoxide, using manual mass flow controllers. The cylinder gases were supplied by BOC and used without further purification. The concentrations of carbon monoxide and carbon dioxide in the gas stream after passage through the reactor tube were measured mass spectrometrically as a function of the temperature of the sample.

2.2.8 Surface area measurements.

(i) "Dead space” measurement

The "dead space" of the apparatus, shown in Fig. 2.6, was measured using helium (99.999%, BOC) at 298 K, as He would not be expected to adsorb onto the sample at 298 K. The measurement was carried out with 0.1g of sample present, so that experiment conditions were reproduced completely. After evacuating the apparatus down to 1×10⁻³ Torr, a small amount of He gas was dosed into V₁ via taps F and C. The pressure p₁ of the gas at V₁ was measured, and then the gas was shared with V₂ via tap A. The resulting pressure p₁⁺₂ was measured, and the gas was shared with V₃ via tap B. The pressure p₁⁺₂⁺₃ was measured. The volumes could then be calculated from the following relations:

\[ p₁V₁ = p₁⁺₂(V₁ + V₂), \]  \hspace{1cm} (2.3)
\[ p₁⁺₂(V₁ + V₂) = p₁⁺₂⁺₃(V₁ + V₂ + V₃), \]  \hspace{1cm} (2.4)

as V₃ is known.
The results are shown in Table 2.1, and these values were used for surface area calculations. The volume $V_3$ had been measured before the experiment by filling with water at 298K and weighing.

Table 2.1 Summary of dead space results for BET apparatus. $V_3$ is known accurately and used to calibrate $V_1$ and $V_2$.

<table>
<thead>
<tr>
<th>Volume of upper cavity, $V_1$/cm$^3$</th>
<th>Volume of upper plus lower cavity, $(V_1 + V_2)$/cm$^3$</th>
<th>Volume of calibration cavity $V_3$/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.5</td>
<td>34.8</td>
<td>24.688</td>
</tr>
</tbody>
</table>

Figure 2.6 Diagram of the apparatus for surface area measurements
(ii) Physisorption: BET

The surface area was measured using the BET method at 77K.
After accurate weighing, in the region of 0.1g of pelletized sample was placed in V₂, evacuated to 1x10⁻³Tor and kept at liquid nitrogen temperature. Kr was used as a probe gas (100.00%, BOC) and an isotherm of minimum of four points was obtained by a succession of dosings.

The calculation of surface area was carried out in the following way. Firstly a thermomolecular flow correction factor was applied to each p₁+₂ [140].

The amount of krypton exposed to the sample surface was calculated from the accumulated p₁'s, using the relation:

\[ n₁ = p₁V₁/RT \]  \hspace{1cm} (2.5)

where pressure is in Pa; T is 298K and V₁ as calculated in dead space measurements.

The amount of Kr in the gas phase at equilibrium was calculated from the corrected p₁+₂'s:

\[ n₁+₂ = p₁+₂(V₁+V₂)/RT, \]  \hspace{1cm} (2.6)

where p₁+₂ is inherently cumulative and T is 77K. Subtracting n₁-n₁+₂ yields the number of moles adsorbed n_ads:

The BET equation:

\[ \frac{p₁+₂/p₀}{n_ads[1-p₁+₂/p₀]} = \frac{1}{n_{mol}C} + \frac{C-1}{p₀n_{mon}C} \]  \hspace{1cm} (2.7)

where p₀ is saturation vapor pressure of krypton at 77K, which is 0.2 kPa [140]; C is a constant and n_{mon} is the amount of Kr adsorbed in a monolayer. n_{mon} was calculated from the plot \{p₁+₂/p₀\}/\{n_ads(1-p₁+₂/p₀)\} over 1/p₀.
The specific surface area, $S_{sp}$, is calculated using the following equation:

$$S_{sp} = \frac{L_{\text{mol}}A_{Kr}}{m} \quad (2.8)$$

where $m$ is the sample mass; $L$ is Avogadro's number, and $A_{Kr}$ is the area occupied by one Kr molecule, which is taken as $20 \times 10^{-20}$ m$^2$ [140].

From the surface area, the average particle size, $r$, can be estimated in the following way*:

$$r = \frac{3}{\rho S_{sp}} \quad (2.9)$$

where $\rho$ is the density, which was taken 6.95 g cm$^{-3}$ for SnO$_2$ cassiterite [141]. This equation assumes spherical particles.

Results of surface area measurements and particle size estimation for SnO$_2$-0.2%Sb starting material are given in Table 2.2.

<table>
<thead>
<tr>
<th>Surface area, $S_{sp}$/ m$^2$/g</th>
<th>particle size, $\rho$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.8</td>
<td>23</td>
</tr>
</tbody>
</table>

* For a spherical particle of radius $r$, the volume $V = \frac{4\pi r^3}{3}$ and surface area $A = 4\pi r^2$. The specific surface area of the pellet is the surface area per unit mass, so to express the mass in terms of particle volume, the density, $\rho$, must be taken into account:

$$A_{sp} = \frac{A}{m} = \frac{A}{V\rho} = \frac{3}{\rho r},$$

Therefore

$$r = \frac{3}{\rho S_{sp}}.$$
2.2.9 Extended X-ray Absorption Fine Structure (EXAFS)

All Ru K-edge X-ray absorption data for this study was obtained on station 9.2 at the Daresbury Laboratory, equipped with a double crystal Si(220) water-cooled monochromator which was offset to 50% of maximum intensity for harmonic rejection. Data was collected in a fluorescent mode for the supported catalysts using a Canberra 13-element Solid State detector. Spectra for the Ru metal and RuO₂ standards and the precursor material was collected in a transmission mode. The beam energy was 2GeV, with an average beam current of ca 200mA.

Ru K-edge data was analyzed using a suite of programs available at Daresbury Laboratory, namely EXCALIB (for converting the raw data to Energy vs absorption coefficient), EXBROOK (for pre-edge subtraction, extraction normalized XANES data and post-edge background subtraction to extract EXAFS data) and EXCURV92 (for detailed curve-fitting analysis of the EXAFS data).


SnO₂-0.2%Sb particle size was measured by transmission electron microscopy on a Phillips 420 STEM system operating in TEM mode at 120kV. TEM samples were prepared by agitating the sample in CCl₄ slurry. Two drops of slurry were applied to a 3mm, 400 mesh, carbon-coated copper grid, which was then briefly dried under a heat lamp. TEM micrographs are given in Fig. 2.7. The particle size for SnO₂-0.2%Sb starting material was estimated to be below 50nm.

The surface morphology of selected samples was studied by scanning electron microscopy using Hitachi s-570 SEM. Samples were gold coated to avoid charging. SnO₂-0.2%Sb starting material, Fig. 2.8, was found to be a well sintered material with narrow distribution of the particle sizes and even porosity.
Figure 2.7 Transmission electron micrograph of SnO$_2$-0.2%Sb sintered powdered sample suspended in CCl$_4$ slurry, bright field image. Arrows indicating single crystallites.

Figure 2.8 Scanning electron micrograph of SnO$_2$-0.2%Sb porous sintered structure.

Electron probe microanalysis (EPMA) linescans of Pt/Sn and Ru/Sn were carried out on JEOL Superprobe JXA-8600 equipped with twin-wavelength dispersive X-ray detectors to study the uniformity of Pt (Ru) distribution within the sensor and in some cases estimation of the metal particle size. Measurements were taken over the 70$\mu$m length with 1$\mu$m steps. The back scattered electron images were also taken.
Chapter 3. Platinized Tin Dioxide.

3.1. Experimental

3.1.1 Preparation

The powdered SnO$_2$-0.2\%Sb, prepared as described in Ch2, was loaded with Pt to produce 3, 6, 10, 12, 25, 50, 100 or 500 \% formal monolayer (ML) Pt coverage, using wetness impregnation. The appropriate mass \% of Pt (Fig. 3.1) was taken each time to form the required monolayer coverage.

![Figure 3.1 Mass \% of Pt taken vs required formal monolayer coverage. Extracted from R. Ridley Ph.D. thesis UCL 1995.](image)

The aqueous tetrammine platinum(II)hydroxide, containing 5g of Pt in 45ml, was added to SnO$_2$-0.2 at\%Sb powdered compound. One drop of Triton x100 was added as a surfactant. The impregnation solution and the support were mixed by hand using a pestle and motor continuously until a completely dry mixture was achieved. Supported samples were then pelletized under 1000kg force in 13mm diameter disks 1-2mm thick and studied. It is known [138] that Pt(NH$_3$)$_4$(OH)$_2$ decomposes to give a highly active catalyst, unlike H$_2$PtCl$_6$ which suffers from the poisoning effects of the residual Cl$^-$ left after decomposition.
3.1.2 Supported materials pretreatment for gas sensitivity measurements.

As described in detail in section 2.2.4, the samples for the gas sensitivity of the electrical resistance measurements were mounted between gold electrodes inside a silica tube in a tube furnace. Prior to electrical resistance measurements the following pretreatments were performed in situ.

**Pretreatment 1.** The pelletized sample was reduced in 10%H₂/N₂ mixture at 340°C for 1 hour to decompose the Pt salt and cooled down to room temperature under above gas mixture. This pretreatment is called "reduction" throughout this report.

**Pretreatment 2.** The pelletized sample was decomposed in pure N₂ at 340°C for 1 hour and cooled down to room temperature in nitrogen. This pretreatment is called "decomposition in N₂" throughout this report.

**Pretreatment 3.** The pelletized sample was calcined in dry air at 340°C for 1 hour to decompose Pt salt and cooled down to room temperature in dry air. This pretreatment is called "decomposition in air" throughout this report.

**Pretreatment 4.** The pelletized sample was decomposed in pure N₂ for 1 hour at 340°C. Without allowing the sample to cool to room temperature it was further oxidized in pure oxygen for further hour at 500°C. The sample was then cooled down in pure oxygen. This pretreatment is called "oxidation" throughout this report. As a result of oxidation at 500°C the sample resistance was increased above the value measurable at room temperature, therefore to allow the resistance measurements to be performed the amount of dopant was increased slightly for this sample to 0.4at%Sb in SnO₂.

Repeated heating of the samples would alter the state of the surface and therefore a new "as prepared" sample was taken each time for a new set of measurements, wherever the decomposition stage was first applied.
3.1.3 Materials characterization.

(i) Gas sensitivity measurements.

The electrical resistance response to carbon monoxide at room temperature was investigated in dry and moist air. Pellets thermally pretreated *in situ* were stabilized in dry air for 10 hours at room temperature and then exposed to increasing concentrations (200, 400, 600, 800, 1000 ppm) of CO in dry air with 1 hour at each concentration. The atmosphere was then changed to moist air of 50% relative humidity (RH) at room temperature (≈20°C) and the CO test program repeated as above.

The CO resistance response as a function of temperature was investigated. Pellets decomposed in air were stabilized in dry air for 10 hours and then exposed to increasing concentrations (200, 400, 600, 800, 1000 ppm) of CO in dry air with 1 hour at each concentration at each of the following temperatures: 30, 60, 80 and 140°C.

(ii) X-ray photo electron spectroscopy

X-ray photoemission spectra were taken on the SnO$_2$-0.2 at%Sb 10%MLPt sample reduced in H$_2$, further exposed to dry air only and finally exposed to air of 50% relative humidity. Thus the sample treatments were chosen to imitate the same conditions as in the resistance measurements. The spectra were also taken on SnO$_2$-0.2%Sb 10%MLPt samples decomposed in N$_2$ and decomposed in air respectively, without their exposure to dry or ambient air. The object of the studies was to establish the surface composition of the sensors to evaluate the level of the surface Pt loading and in particular to determine the chemical state of Pt on the surface after subjecting the samples to different treatments.
The sample "as prepared" was mounted onto the sample holder used for XPS analysis and placed in a glass tube positioned in a tube furnace. The glass tube was connected to an enclosed circulation system and the sample on the holder was decomposed under required conditions at 340°C for 1 hour and allowed to cool to room temperature.

Under nitrogen the sample was then mounted into the ESCALAB chamber and the first x-ray photoemission spectra taken. The sample was then transferred back into glass tube under nitrogen and exposed to dry air over night, prior to second XPS measurements. Finally the sample was exposed to moisture in air over night and the third spectra taken.

C 1s was used as the binding energy reference, using a value of 284.8eV [139]. Atomic analyses of the sample surface were carried out by measuring the relative peak areas for Sn 3d, O 1s, Pt 4f, Sb 3d and C 1s and expressing them in terms of percentage atomic concentration. Curve fitting, using linear background, was applied in the Pt 4f region to enable separation of spectra into constituent peaks and therefore allow assignment. In the Pt 4f region of the spectrum the \( \frac{4f_{7/2}}{4f_{5/2}} \) peak ratio was set to 4.3 and the \( (4f_{7/2} - 4f_{5/2}) \) binding energy difference to 3.2 eV [139]. Peak assignment was made as follows [142,143]: Pt\(^0\) -metal- (~71eV), Pt\(^2+\) -PtO or Pt(OH)\(_2\) (~73eV), Pt\(^4+\) -PtO\(_2\) (~75eV).

(iii) Temperature Programmed Decomposition (TPDE).

Temperature programmed desorption (TPD)

The methods have been described in Ch2. TPDE spectra were recorded on initial heating of the samples to study decomposition of the Pt salt used to decorate the surface. The spectra were recorded for mass 18 (H\(_2\)O\(^+\)), 28 (CO\(^+\)), 44(CO\(_2\)\(^+\)), 2 (H\(_2\)), 16 (O) and 17, 15 (ammonia) with heating rate of 20°/min from room temperature to 450°C. TPD studies were performed at ambient pressure in a closed circulating system. Impregnated samples were decomposed at 340°C under 20% O\(_2\) in a flow of He and cooled down to room temperature. For CO TPD this decomposed sample was exposed to pure CO for 5 min at room temperature, the cell was then purged with pure He and the temperature was ramped at 30°/min to 450°C.
(iv) Catalytic CO oxidation over Pt decorated SnO$_2$-0.2%Sb.

Combustion of CO over the two SnO$_2$-0.2%Sb 10%MLPt samples, decomposed in air and reduced, were compared. Following the sample decomposition \textit{in situ} under the appropriate atmosphere and cooling down to room temperature, the test gas mixture of 700ppm CO in 20%O$_2$-80% He was passed through the sample bed at room temperature. The concentration of CO in the gas mixture was increased in 700ppm steps to 2100ppm with 15 min at each step still at room temperature. The exit gas mixture was monitored every 3 sec to test the combustion taking place at room temperature. Finally, in the last gas mixture, the temperature of the sample was ramped to 450$^\circ$C at 30$^\circ$/min.

(v) Pt particle size measurements by CO chemisorption.

To find the surface area of the platinum on the tin dioxide, the same method and apparatus was used as for the BET experiments. The difference was that only one adsorption point was obtained, and the experiment was carried out using pure CO (100.00%, BOC) at 298K. The platinum surface area was simply calculated from the measured CO adsorption, as CO does not adsorb, to any significant degree, on SnO$_2$ at 298K [109].

The amount of CO adsorbed, $n_{\text{ads}}$, was calculated in the same way as for BET measurements, i.e. using ideal gas law. In this case, as it is chemisorption we are dealing with, not physisorption, it can be assumed that $n_{\text{ads}}= n_{\text{mon}}$. The specific surface area can then be calculated using the equation:

$$S_{sp}= \frac{L_{\text{ads}}A_{\text{co}}}{m} \quad (3.1)$$

where $A_{\text{co}}$ is the area occupied by one CO molecule and is taken as $16x10^{-20}$ m$^2$ [141]; m is the mass of the whole sample.
This method assumes that CO is adsorbed in a close packed monolayer, and this is somewhat of a simplification. Although CO coverages equivalent to a full monolayer have been observed, to obtain such a high coverage, the metal had to be cooled to well below room temperature. At room temperature, the coverage is significantly lower due to CO-CO repulsions. In fact, at 300K, the saturation CO coverage on Pt(III) has been observed to be 0.5 ML [90,91]. The above surface area was therefore multiplied by a factor of two in order to obtain a better estimate of real surface area.

The average apparent platinum particle size was estimated from the specific surface area using the equation*:

\[
r = \frac{3w_{Pt}/\rho_{Pt}S_{sp}}{S_{sp}}
\]

(3.2)

where \( w_{Pt} \) is the mass of added Pt per unit mass of composite, and \( \rho_{Pt} \) is the density of platinum which is 21.45 g cm\(^{-3} \) [141].

* The equation can be derived similarly to eqn. (2.9). Although the Pt particles are more likely to resemble hemispheres than spheres, the factor of \( \frac{3}{2} \) would be canceled out. The difference is that here the surface area of only a fraction of the sample is measured. To account for this, the relative mass of the platinum is included.
3.2 Results.

3.2.1 TPDE

Decomposition of tetrammine platinum(II) hydroxide appeared to take place at 200°C (Fig 3.2). The higher temperature TPR signals correspond to decomposition of Triton x100, which was added to the powders as a surfactant. A temperature of 300°C achieved full decomposition of organic additives.

Figure 3.2 Temperature programmed decomposition spectra of the precursor Pt complex (Pt(NH$_3$)$_4$(OH)$_2$) and the surfactant (triton 100), recorded for the impregnated sample of SnO$_2$-0.2%Sb: 1-CO', 2-NH$_3^+$, 3-H$_2$O, 4- O$_{16}^-$, 5-CO$_2^-$, 6-H$_2$
3.2.2 Resistivity measurements.

The plot of the resistivity vs Pt loading, obtained under constant manual force of 300kg, for SnO$_2$-0.2%Sb based samples decomposed in N$_2$ is given in Fig. 3.3. On Pt loading up to about 10%ML a resistivity increase was observed, followed by a decrease on further Pt loading. Note that around 50%ML the resistance value was close to that for metal free oxide. Higher loading of Pt, beyond this level, caused a steep drop in the resistivity.

![Figure 3.3 Electrical resistivity at a constant force of 300kg of SnO$_2$-0.2%Sb Pt decorated porous pellets, decomposed in N$_2$, as a function of Pt loading: resistivity $\rho$ is plotted against formal Pt monolayer coverage.](image)

3.2.3 Electron Probe Microanalysis: Pt particle size estimation

Fig. 3.4. shows secondary electron image and backscattered electron image of the same area of the surface of SnO$_2$-0.2%Sb based sample with 100%ML Pt loading, decomposed in N$_2$. The lighter Pt areas can be easily observed in the backscattered electron image. Electron probe microanalysis linescans were performed across the area of Pt agglomerations to estimate Pt particle size. The intensities of both Sn and Pt wavelength-dispersive X-rays signals were recorded simultaneously as a function of position and the results are presented in Fig. 3.5.
Figure 3.4 Scanning electron micrograph of the surface of the SnO₂-0.2%Sb porous pellet decorated with a Pt coverage of 100% formal monolayer, decomposed in N₂ (a). Back scattered electron image of the same area of the surface (b).

Figure 3.5 Electron probe microanalysis linescans of Pt and Sn over 70μm with 2μm steps for the SnO₂-0.2%Sb porous pellet decorated with a Pt coverage of 100% formal monolayer, decomposed in N₂.

At the peak point in the intensity of Pt signal there is a mirror decrease in the intensity of Sn signal, with a peak width of about 5 μm signifying an average size of Pt particle, probably an agglomerates. Pt particle size for the sample with 10%ML coverage was measured by CO chemisorption (see paragraph 3.2.7). Table 3.1 summarizes estimated Pt particle size for samples with 10 and 100% ML Pt coverage obtained by CO chemisorption and electron probe microanalysis respectively.
Table 3.1 Pt particle size for SnO$_2$-0.2%Sb samples with 10% and 100% ML Pt coverage.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_{Pt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%ML Pt</td>
<td>5(\mu)m (EPMA)</td>
</tr>
<tr>
<td>10%ML Pt</td>
<td>2.8nm (CO adsorption)</td>
</tr>
</tbody>
</table>

3.2.4 Gas sensitivity measurements on SnO$_2$-0.2%Sb 10%ML Pt

(i) Reduced samples.

Reduced samples showed good room temperature CO resistance response in air with relative humidity 50% (Fig. 3.6). However, there was a complex and interesting interaction between the effects of CO and those of water vapor, as shown in Fig 3.6. Initially dry samples were almost insensitive to CO. Then, after an exposure to moisture, a CO resistance response in dry air of similar magnitude to that in moist air could be observed. Thus, the development of a response to CO seemed to require a hydration of the surface, which persisted even though the water content of the atmosphere was subsequently removed. This apparent hydration of the surface was also reflected in changes in the baseline resistance (Fig 3.6). After an instant resistance decrease on the first exposure to moisture, the baseline resistance of the sample slowly increased. Then, when the atmosphere was switched back to dry air, the baseline resistance rapidly increased even further, to a value considerably higher than that of the starting dry material. This effect was only observed following the very first exposure of the material to water vapor. In the subsequent dry air -wet air cycles the baseline resistance remained more or less stable for a given ambient atmosphere, decreasing in response to an increase of water vapor pressure.
Figure 3.6 Time profile of the room-temperature resistance of the reduced SnO$_2$-0.2%Sb Pt decorated (10%ML) porous pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.

Figure 3.7 Time profile of the room-temperature resistance of the reduced SnO$_2$-0.2%Sb porous pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.
For the reduced tin-antimony oxide sample without Pt the complex effect of moisture exposure on the base line resistance was not observed (Fig 3.7). The base line simply decreased in response to increase of water vapor pressure. The resistance was not sensitive to CO at room temperature. The apparent effect of first exposure in dry air was small and indistinct and may have been due to a small change in the moisture content of the gas stream. The resistivity of the platinized samples at first was much less than that of the unplatinized material, but after the cycles of exposure to water vapor, the resistivity of the two samples were similar.

(ii) Nitrogen decomposed samples

The pattern of the base line resistance response to moisture exposure and of the resistance response to CO in dry and moist air, of the sample decomposed in pure Nitrogen was identical to that of the reduced samples (plot a & b, Fig 3.8). The resistivity, however, was some 100 times greater.

(iii) Air decomposed samples

The sample decomposed in air (Fig 3.8, plot c) behaved very differently to those which had been decomposed in an oxygen free atmosphere. Firstly, the baseline resistivity in dry air at room temperature was more than 100 times greater than that of the nitrogen decomposed sample. Secondly, there was a large room temperature CO resistance response on the very first exposure in dry air. The resistance response to CO was significantly smaller in moist air than in dry air. There was a large resistance response to the presence of moisture in the air. This behavior was reproducible on the subsequent dry air-moist air cycle. Note also that in moist air the resistance appeared to oscillate when CO was applied.
Figure 3.8 Time profile of the room-temperature resistance of the Pt decorated (10%ML) SnO$_2$-0.2%Sb porous pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air: reduced sample (a), N$_2$ decomposed sample (b), dry air decomposed sample (---) (c).
(iv) Oxidized sample

Plot of the resistance response to CO in wet and dry air for the oxidized Pt supported sample is given in Fig. 3.9. The pattern of the CO resistance response was similar to that of the sample decomposed in air. A large resistance response was observed on initial exposure of the dry sample to CO, reduced on exposure to moisture. Resistance oscillations in humid air when CO was applied were also observed. The resistance response to moisture, and the difference between wet and dry CO response, were smaller than that of the sample decomposed in air. There may have been a slightly higher dopant concentration than that in the sample decomposed in air, reflected in a lower baseline resistance in dry air.

Figure 3.9 Time profile of the room-temperature resistance of the oxidized SnO$_2$-0.2%Sb Pt decorated (10%ML) porous pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.
(v) CO response law:

A double logarithmic plot, demonstrating the power law dependence on CO concentration of the resistance response, $S$, in dry and wet air for the three samples: decomposed in $N_2$, decomposed in air and reduced is given in Fig. 3.10, if the dependence is assumed to be of a form:

$$\sigma = \sigma_0 (1 + \kappa P_{CO}^\beta)$$

(3.1)

where $\kappa$ is sensitivity and $\beta$ is the response exponent. Hence:

$$\log S = \log \frac{\sigma}{\sigma_0} = \log \kappa + \beta \log[CO]$$

(3.2)

Note that for each sample the power law concentration dependence of the response remained unchanged in wet and dry conditions.

![Figure 3.10 Log-log plot of the room-temperature resistance response ($S = \Delta\sigma/\sigma_0$) versus CO concentration, ppm in dry (---) and wet (— ) air, for the SnO$_2$-0.2% Sb Pt decorated (10% ML) pellets: (●) reduced, (○) $N_2$ decomposed and (□) dry air decomposed. log S is plotted against log$P_{CO}$. The gradient is equal to the response exponent (see text).](image-url)
The CO sensitivity, $\kappa$ for the three samples is given in Table 3.2. These values refer to gas response after the first exposure to moisture: for the air decomposed sample this comment is not important, but for the reduced sample it is, since this sample showed no response at all in dry air until it had first been exposed to water vapor.

Table 3.2 CO sensitivity, $\kappa$ in wet and moist air for SnO$_2$-0.2%Sb 10% ML Pt samples of various pretreatments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\kappa_{\text{dry CO/ppm}}$</th>
<th>$\kappa_{\text{wet CO/ppm}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposed in air</td>
<td>51.78</td>
<td>5.56</td>
</tr>
<tr>
<td>Decomposed in $N_2$</td>
<td>1.57</td>
<td>1.69</td>
</tr>
<tr>
<td>Reduced</td>
<td>0.85</td>
<td>0.97</td>
</tr>
</tbody>
</table>

For the two samples pretreated in oxygen free atmosphere the values for the CO sensitivity were very close and in the region 1-2. There was no difference between the values of the sensitivity to wet and dry CO. The sample decomposed in air shows rather high sensitivity of about 5 to wet CO, which is in turn was one order of magnitude lower than that to dry CO. The response exponent, $\beta$, was approximately 0.5 for the air-decomposed sample but much smaller, $\approx 0.1$, for the samples decomposed in the absence of oxygen.

(vi) Temperature dependence.

The experimental data for resistance variation with time as a function of temperature and CO concentration for the air-decomposed sample is given in Fig. 3.11. An increase in temperature from 30 to 50°C caused no change in the CO resistance response of the material. A slight decrease in the base line resistance can be noted due to the temperature increase. However, on further temperature increase to about 100°C a considerable loss in sensor response to CO was recorded, and for the temperatures above 100°C no CO resistance response was observed at all.
Figure 3.11 Time profile of the resistance of the air decomposed SnO$_2$-0.2%Sb Pt decorated (10%ML) porous pellet as a function of temperature as shown, and exposure to ppm concentrations of CO in dry air at each temperature.

At each temperature the value of the base line resistance was compared to that of a metal free SnO$_2$-0.4%Sb pellet, tested in an analogous fashion. The results are summarized in Table 3.3

Table 3.3 Comparison of resistivities $\rho$ for SnO$_2$-0.4%Sb sample and SnO$_2$-0.4%Sb sample with 10% ML Pt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho/\Omega$ m, 30°C</th>
<th>$\rho/\Omega$ m, 50°C</th>
<th>$\rho/\Omega$ m, 100°C</th>
<th>$\rho/\Omega$ m, 140°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% ML Pt</td>
<td>59251</td>
<td>58876</td>
<td>9708</td>
<td>6811</td>
</tr>
<tr>
<td>0% ML Pt</td>
<td>2690</td>
<td>3005</td>
<td>712</td>
<td>672</td>
</tr>
</tbody>
</table>

Note a higher value of resistivity at all temperatures for the platinized sample, compared to that for the metal free sample.
Activation energies for the conductivity of the two samples were estimated from slope of the Arrhenius plot of $\ln \sigma$ vs $1/T$ (Fig 1.12) and the values are summarized in Table 3.4.

Table 3.4 Activation energies, $E_a$, for the conductivity for SnO$_2$-0.4%Sb sample and SnO$_2$-0.4%Sb sample with 10% ML Pt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_a$/J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% ML Pt</td>
<td>2829</td>
</tr>
<tr>
<td>0% ML Pt</td>
<td>1918</td>
</tr>
</tbody>
</table>

Note increase in the activation energy for the Pt modified sample.

Figure 3.12 Temperature dependence of electrical conductivity of air decomposed SnO$_2$-0.2%Sb samples with ■ - 0%ML Pt and □ - 10%ML Pt: conductivity, $\ln \sigma$, against temperature, $1/T$. 
3.2.5 X-ray Photoelectron Spectroscopy.

(i) Reduced samples

Valence band region:

X-ray excited photoemission spectra in the valence band region for the reduced platinized and unmodified SnO$_2$-0.2%Sb samples are given in Fig. 3.13. Both samples were subjected to ambient humidity. An identical spectrum for the two samples between 4 and 14eV was observed. This corresponds to the SnO$_2$ valence band, constructed of Sn 5s and O 2p components. Energy states within the band gap, ca 2.0eV below the Fermi level, are evident for the platinized sample, absent in the unplatinized sample. Those states have been assigned to Pt surface states. Similar near-Fermi level peaks due to Pt surface states have been reported for ultraviolet photoelectron spectroscopy studies on Pt by Collins et al. [91] and for Pt on Al$_2$O$_3$ by Altman et al. [102]. A shift in the valence band maximum of ca 0.4eV towards lower binding energy was found for the platinized sample, compared to the unmodified sample.

![Figure 3.13 Valence band spectra of pure (a) SnO$_2$-0.2%Sb and (b) SnO$_2$-0.2%Sb impregnated with 10% ML Pt. Both samples were reduced and exposed to ambient atmosphere.](image)
Changes in the valence band spectrum of the newly reduced platinized sample, induced by exposure of the sample to dry air and subsequent exposure to 50% relative humidity in air were investigated. A sample of the metal free SnO$_2$-0.2%Sb was likewise reduced, subsequently exposed to dry air, followed by moist air. The XP spectra were recorded at each step for the two samples and the changes in the valence band region are compared in Figures 3.14 & 3.15. A decrease in the intensity at ca 1.0eV above the valence band edge was characteristic for the spectra of both platinized and metal free reduced samples on exposure to dry air. Lau et al [144] reported an ESCA study of oxidation of tin. The VB edge of SnO was recorded at 2eV. Evidently the sample reduction resulted in the formation of Sn$^{2+}$ surface states within the band gap. On exposure to dry air Sn$^{2+}$ was oxidized to Sn$^{4+}$ and those states were removed. However further loss in intensity at the valence band edge on exposure to moist air was only noted for the platinized sample.

![Figure 3.14 Valence band spectra of SnO$_2$-0.2%Sb impregnated with 10% ML Pt recorded (a) after reduction, (b) following exposure to dry air, (c) subsequent exposure to air of 50% relative humidity.](image)
Figure 3.15 Valence band spectra of pure SnO$_2$-0.2%Sb recorded (a) after reduction, (b) following exposure to dry air.

**Pt 4f core region:**

Fig. 3.16 (a-c) shows XP spectra within Pt 4f region for an initially reduced sample, the same sample exposed to dry air overnight, and finally the sample after overnight exposure to air of 50% relative humidity. The Pt 4f signal of the reduced sample is characterized by a single peak at 71.6 eV, assigned to Pt$^0$ species. Exposure of the sample to dry air caused no change in the Pt 4f XP spectra: a single peak of constant FWHM (1.2 eV) was still sufficient to fit the region. In both cases therefore only metallic Pt surface species were present. However, on exposure of this platinized sample to moist air a broadening of the Pt 4f core level peak towards higher binding energies took place. A small peak at 73.4 eV can be clearly observed, signifying partial oxidation of Pt$^0$ surface species to Pt$^{2+}$. Note that the exposure to moisture of the dry reduced sample was necessary for the development of the CO resistance response at room temperature.
Figure 3.16 XP spectra of the Pt 4f region for SnO$_2$-0.2%Sb 10%ML Pt porous pellet recorded (a) after reduction, (b) following exposure to dry air, and (c) subsequent exposure to air with 50% relative humidity.


**Surface composition:**

The amount of both Sb and Pt detected at the surface with XPS probe remained constant for the reduced platinized sample after decomposition and during dry air exposure. No significant change was observed after wet air exposure either: Table 3.5.

**Table 3.5 Surface Pt and Sb contents for SnO₂-0.2%Sb Pt modified**

<table>
<thead>
<tr>
<th>Sample treatment</th>
<th>[Pt]/[Sn+Pt+Sb]%</th>
<th>[Sb]/[Sb+Pt+Sn]%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced in H₂/N₂</td>
<td>1.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Exposed to dry air</td>
<td>1.1.</td>
<td>2.2</td>
</tr>
<tr>
<td>Exposed to moist air</td>
<td>1.2</td>
<td>1.7</td>
</tr>
</tbody>
</table>

(ii) **Samples decomposed in nitrogen and air.**

**Pt 4f core region:**

Fig 3.17 shows the X-ray excited photoemission spectrum of the Pt 4f region of the sample decomposed in N₂, compared with that of the reduced sample. Fig 3.18 shows the Pt 4f core level spectrum for the sample decomposed in dry air. The spectra for the reduced and N₂ decomposed samples were very similar, with a distinct peak at 71.6 eV. In the XP spectrum of the sample decomposed in air, however, there were two peaks of similar intensity in the Pt 4f region with binding energies 71.3 and 73.4 eV, signifying the presence of both Pt⁰ and Pt²⁺. This sample showed a very high CO sensitivity initially in dry air.

![Figure 3.17 XP spectra of the Pt 4f region for (a) reduced and (b) N₂ decomposed SnO₂-0.2% Sb 10% ML Pt pellets.](image)
Figure 3.18 XP spectrum of the Pt 4f region for air decomposed SnO$_2$-0.2%Sb 10%ML Pt porous pellet.

Surface composition:

The surface composition for the three samples is given in Table 3.6

Table 3.6 Pt and Sb surface content for SnO$_2$-0.2%Sb 10% ML Pt samples for various pretreatments

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Pt]/[Sn+Pt+Sb]%</th>
<th>[Sb]/[Sb+Pt+Sn]%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$N$_2$ decomposed</td>
<td>0.87</td>
<td>2.4</td>
</tr>
<tr>
<td>N$_2$ decomposed</td>
<td>1.0</td>
<td>1.7</td>
</tr>
<tr>
<td>dry air decomposed</td>
<td>1.2</td>
<td>2.4</td>
</tr>
</tbody>
</table>

The Pt and Sb surface content of the three samples appeared to be the same within the experimental error.
3.2.6 Scanning Electron Microscopy

SEM micrographs of the surface of the three samples: decomposed in N$_2$, decomposed in air and reduced are given in Fig 3.19 (a-c). The microstructure of the sample decomposed in air was characterized by a narrow particle size distribution and even necking and porosity. An increase in the degree of agglomeration was observed for the sample decomposed in N$_2$. Rather large agglomerates were found in the microstructure of the reduced sample.

![SEM micrographs](image)

Figure 3.19 Scanning electron micrographs of (a) air decomposed, (b) N$_2$ decomposed, and (c) reduced SnO$_2$-0.2%Sb Pt loaded (10%ML) pellets.
3.2.7 Surface area and Pt particle size measurements.

BET surface area measurements were performed of the three samples decomposed in $N_2$, decomposed in air and reduced and the results are summarized in the Table 3.7.

Table 3.7 BET surface area, $S_{sp}$, for SnO$_2$-0.2%Sb 10%ML Pt samples for different pretreatments.

<table>
<thead>
<tr>
<th>Sample pretreatment</th>
<th>$S_{sp}$/m$^2$g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry air</td>
<td>21.2</td>
</tr>
<tr>
<td>$N_2$</td>
<td>11.9</td>
</tr>
<tr>
<td>$H_2$ (10% in$N_2$)</td>
<td>7.4</td>
</tr>
</tbody>
</table>

The sample decomposed in air had the highest surface area, which was lowered by about half for the sample decomposed in $N_2$ and even further lowered, however by not as much, for the reduced sample. The surface area measurements correlate with the observed differences in the microstructure.

Pt particles sizes were estimated for the above three samples by CO chemisorption and the results are given in the Table 3.8.

Table 3.8 Pt particle size, $\rho_{pt}$, for SnO$_2$-0.2%Sb 10% ML Pt samples for different pretreatment.

<table>
<thead>
<tr>
<th>Sample pretreatment</th>
<th>$\rho_{pt}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry air</td>
<td>1.2</td>
</tr>
<tr>
<td>$N_2$</td>
<td>2.8</td>
</tr>
<tr>
<td>$H_2$ (10% in$N_2$)</td>
<td>3.2</td>
</tr>
</tbody>
</table>

First of all note that all pretreatments produced ultrasmall Pt particles of a few nanometers dimension. On the other hand decomposition in $N_2$ resulted in an increase over twofold in the particle size of the supported Pt compared to that produced on decomposition in air.
Note the apparent link between the increase in the size of supported particles and the observed decrease in the surface area. The difference in Pt particle size obtained on decomposition in N\textsubscript{2} and on reduction, however, was not significant, despite their different surface area.

3.2.8 Catalytic CO oxidation and Temperature Programmed Desorption of CO

Fig. 3.20 shows time profiles of mass spectrometer signals for mass 28(CO\textsuperscript{+}) and 44(CO\textsubscript{2+}) recorded during the progress of catalytic CO oxidation over the dry reduced sample. Carbon monoxide combusted fully over the dry reduced material even at room temperature, since no CO signal could be detected above the background. An increase in CO concentration in the gas stream at room temperature simply resulted in more CO\textsubscript{2} being produced, with no increase in CO signal intensity. On sample heating no further increase in CO\textsubscript{2} signal intensity was observed, signifying full CO oxidation at room temperature. Note that the dry reduced sample was not sensitive to CO at room temperature.

![Figure 3.20 Time profiles of mass 28 (CO\textsuperscript{+}) and mass 44 (CO\textsubscript{2+}) exhaust gas intensities upon exposure of reduced SnO\textsubscript{2}-0.2%Sb 10%Pt powder to 0, 700, 1400 and 2100 ppm CO in synthetic air (20%O\textsubscript{2}, 80%He) mixture followed by a temperature ramp at 30°C/min from 25°C.](image-url)
Fig. 3.21 shows time profiles of mass spectrometer signals for mass 28(CO) and 44(CO$_2$) recorded during catalytic CO oxidation over the dry sample decomposed in air. It is apparent that CO combustion was negligible over the sample at room temperature. An increase in CO concentration in the gas stream at room temperature was reflected in an increase in the CO signal intensity and no CO$_2$ evolution could be detected above background. On sample heating the onset of combustion was found to be around 60°C, characterized by a sharp positive step in CO$_2$ evolution and a drop in CO signal intensity. Furthermore, a large CO$_2$ desorption-like peak was found around 90°C. This was observed repeatedly and is not an artifact. There was no corresponding feature in the CO consumption signal, signifying that the excess CO$_2$ evolved could be due to oxidation of CO chemisorbed onto sample surface during the room temperature exposure. Note that the temperature of onset of CO$_2$ combustion corresponded to a loss of the gas sensing response in the study of the response as a function of temperature.

Figure 3.21 Time profiles of mass 28 (CO) and mass 44(CO$_2$) exhaust gas intensities upon exposure of air decomposed SnO$_2$-0.2%Sb 10%Pt powder to 0, 700, 1400 and 2100 ppm CO in synthetic air (20%O$_2$, 80%He) mixture followed by a temperature ramp at 30°C/min from 25°C.
Fig. 3.22 illustrates the TPD time profile in flowing He obtained over the sample decomposed in air and pre-exposed to CO at room temperature. Only CO$_2$ was observed in the TPD spectra, measured mass spectrometrically. There was no oxygen present in the gas stream, thus it is apparent that CO chemisorbed onto the sample surface oxidized via the reaction with surface oxygen adatoms and evolved as CO$_2$. The temperature of CO$_2$ desorption onset was around 90$^\circ$C, which correlates well with the temperature of the desorption-like CO$_2$ peak observed in Fig. 3.20.

Figure 3.22 TPD profile in flowing He for air decomposed SnO$_2$-0.2%Sb 10%ML Pt powder pre-exposed to CO at room temperature.
3.3 Discussion.

It is apparent that the gas sensing mechanism cannot be explained by CO combustion, as in the case of metal free SnO$_2$ [39,55]. In the case of the dry reduced sample CO oxidation took place at room temperature and no CO resistance response was observed. On the other hand the sample decomposed in air showed high CO sensitivity at ambient temperature below an onset of combustion. CO appeared to adsorb onto the sample surface at room temperature in the TPD studies. We also demonstrated that at temperatures high enough for surface catalyzed combustion to occur the CO resistance response was diminished. In the interpretation which follows we demonstrate that the conductivity of the sensor is controlled by an oxidation state of supported Pt and that the observed room temperature CO response is specifically due to CO chemisorption onto particular Pt surface states.

Platinum modifies the valence band structure of pure SnO$_2$, creating extra electronic states within the band gap, 0.5eV below the Fermi level, which results in a band bending of 0.4eV, as demonstrated by XPS. There evidently seems to be a direct electronic interaction between the Pt additives and the tin dioxide support. The higher resistivities recorded for platinized samples at low Pt loading (up to 10%) compared to metal free samples are therefore due to electron exchange between the tin dioxide support and surface Pt states rather than chemisorbed oxygen trap states associated with SnO$_2$.

To observe the effect on conductivity, the Pt dispersion over the support surface should be uniform, so the depletion layers around each particle overlap [83]. The decrease in resistivity observed on the increase in Pt loading above 10%ML is attributed to partial agglomeration of Pt particles and therefore lower dispersion. This would result in the proportion of the conduction paths due to pure tin dioxide intergranular contacts to increase. Thus at 50% ML the resistivity was that of metal free SnO$_2$. Further increase in Pt particle size to 5μm, as seen on the microprobe, could result in the formation of low resistance paths through the Pt particles themselves, which would explain the sharp drop in resistivity at higher loadings.
On initial exposure of the reduced sample to humid air the gradual base line resistance increase was found only for the Pt decorated sample and was not observed for the metal free sample. Exposure of the sample to moisture also resulted in partial oxidation of the metallic Pt to Pt$^{2+}$, recorded as a positive Pt 4f binding energy shift. It is suggested that formation of electron deficient Pt$^{2+}$ states results in a charge transfer between the Pt particles and tin dioxide support, and is measured as a resistance increase. In fact the changes in electronic structure at the valence band edge caused by exposure to moisture were only observed in the VB spectra of the sample loaded with Pt. The sample conductivity therefore is dependent on the oxidation state of supported Pt.

The interaction of water with the tin dioxide surface has been extensively studied and is well documented [43,62, 131]. Authors agree that water adsorbs dissociatively onto SnO$_2$ resulting in the formation of two hydroxyl groups, one from water molecule dissociation and the other from the reaction between the hydrogen and the lattice oxygen. In the case of Pt loaded SnO$_2$ at the metal-semiconductor interface there is a possibility of the formation of hydroxyl groups bound to Pt from the reaction between hydrogen and oxygen chemisorbed onto the Pt surface, as well as, or rather than the tin dioxide lattice oxygen. Such Pt hydroxyl groups could then recombine and desorb as molecular water [145,146]. This effect is somewhat similar to the titration of Pt chemisorbed oxygen and is highly exothermic:

$$\Delta H = -225 \text{ kJ/mol}$$ [147]. One can then suggest that in the vicinity of the metal-support interface the heat of the reaction drives the partial oxidation of Pt metal particles on exposure of the dry sample to moisture. The kinetics of oxidation on the surface of Pt are slow [148] and evidently to achieve a sensor with a stable base line it is sensible to preoxidize the surface prior to operation. We have seen that the oxidized sample showed no resistance drift in humid air.

The presence of oxidized Pt species evidently plays a dominant part in the low temperature gas sensing mechanism of Pt loaded tin dioxide. Thus exposure to moisture of the dry reduced sample was necessary for the room temperature CO response to be observed, and we have shown that moisture exposure resulted in partial oxidation of metallic Pt to Pt$^{2+}$. 

The sample decomposed in air showed high CO sensitivity and a 50% oxidation of the surface Pt. The room temperature CO response was further increased after an even more severe oxidation of the sample (in oxygen at 500°C). The proposed mechanism of the room temperature CO response is therefore that of CO chemisorption onto specific Pt$^{2+}$ active surface sites.

The standard model for CO bonding to metallic Pt [87,149] is σ donation from the highest occupied CO 5σ orbital to the empty metal orbital of suitable symmetry, followed by π back-donation from the metal to carbon monoxide π* orbital. The two components are synergically related and both theoretical and experimental findings show that CO-Pt bond is essentially electroneutral [150]. No change in the work function [90] and a value of 0.07eV [91] for the work function change on CO chemisorption onto Pt surface with a high density of defects has been reported. Ultrasmall Pt particles can be characterized by high surface defect density such as edges and steps [89], thus those results are appropriate for our system.

Now in air we deal with oxygen precovered metallic Pt particles and oxygen chemisorption results in Pt work function variation of +0.55eV [90]. Therefore it is unlikely that CO chemisorption onto oxygen precovered Pt surface would produce variation in free-electron equilibrium within a Pt particle. On the other hand CO adsorption might proceed via substitution of chemisorbed oxygen species, thus causing a work function decrease. This hypothesis, however contradicts a large number of findings [151-153], which unanimously agree that on a dense oxygen covered Pt surface there still exist sites for CO adsorption. Therefore, for the tin dioxide sensor decorated with metallic Pt particles no electrical signal could be expected in air on CO chemisorption.

In a number of IR studies of CO adsorption onto supported platinum [154-156] typically three bands were reported of frequency 2060cm$^{-1}$, 2130cm$^{-1}$ and 2180cm$^{-1}$. Those were generally assigned to Pt$^0$-CO linear carbonyls (typical for Pt surface of high defect density), Pt$^{2+}$-CO and Pt$^{4+}$-CO respectively. The increase in C-O stretching reported for Pt$^{2+}$-CO, compared to Pt$^0$-CO signifies strengthening of the C-O bond. Increase in the
\( \pi \) back-donation of metal electrons into \( 2\pi \) CO antibonding orbitals would result in the weakening of the C-O bond, whereas increase in the \( \sigma \) bond order, involving the CO \( 5\sigma \) orbital, which is slightly antibonding, would cause C-O bond strengthening. Therefore, based on the IR results, CO is evidently bound to Pt\(^{2+}\) cations mainly by \( \sigma \) bonding. Indeed \( \sigma \) donation from CO to metal, when the latter is in +2 oxidation state does not lead to such an unacceptable concentration of electron density on the metal atom. Electron depleted Pt\(^{2+}\) surface states act as a Lewis acid and the reaction between Pt\(^{2+}\) and CO can be considered as a redox interaction. The conductivity, as we have shown, is controlled by an oxidation state of supported Pt. Decrease in the Lewis acidity of the Pt\(^{2+}\) site on CO chemisorption, and thus partial Pt reduction, is measured as a conductivity increase.

Hadjiivanov et al.[157] demonstrated that on the water precovered surface the band due to Pt\(^{2+}\)-CO could still be observed, whereas the band at 2186\( \text{cm}^{-1} \) due to Pt\(^{4+}\)-CO disappeared on exposure to water vapor. He suggested that water, being a strong base, substitutes carbonyls bound via \( \sigma \) bond only. For Pt\(^{2+}\) cations he assumed the same order of magnitude for the heat of CO and H\(_2\)O adsorption: the metal-CO bond for the case of Pt\(^{2+}\) would be stronger compared to Pt\(^{4+}\) due to some degree of \( \pi \) back donation in the former bonding. In the case of the oxidized sample and the one decomposed in air we observed resistance oscillations when CO was applied in moist air. If, as a result of oxidation and decomposition in air, some Pt\(^{4+}\) species were formed then the observed resistance oscillations could be interpreted as due to the competition of water and CO for those adsorption sites.

Exposure to moisture of the dry sample decomposed in air caused a dramatic conductance increase. An increase in the number of charge carriers resulted in the effects caused by variations in electronic state of surface Pt to be less pronounced. Thus a decrease in CO sensitivity was observed in moist air.
Large increases in gas sensitivity of the sample decomposed in air compared to the other two decomposed under an oxygen free atmosphere can not be fully attributed to an increase in the degree of Pt oxidation and is indeed mainly due to the differences in their microstructure, such as higher surface area and finer Pt particles of the former. Samples of high surface area are characterized by high surface-to-bulk ratio and therefore a larger proportion of the volume of the sample is affected by surface processes. Further, it appears that the support with the larger surface area stabilized smaller Pt particles, implying higher Pt dispersion. Henshaw et al [109] interpreted the conductance in the platinized tin dioxide pellets in terms of a three phase (gas-SnO2-Pt-SnO2) percolation model, which allowed them to account for the microstructure and Pt dispersion dependent room temperature resistance response of the material. Three different resistance elements were distinguished to model the platinized tin dioxide system, each having a random spatial distribution: $R_1$ was identified as gas-sensitive surface area at room temperature, or the structure domains whose resistance is controlled by the surface state of the Pt; $R_2$ was identified as gas-insensitive surface area at room temperature, or the fraction of the free surface of the grains unaffected by electronic properties of the Pt; and $R_3$ was assumed to represent the interior of crystallites and agglomerates, unaffected by surface processes. The relative contributions of the individual resistance elements to total electrical resistance of the model system was varied by changing the initial conditions of Pt loading and porosity. In the limiting case, when only particles of type 1 were present the power law response of order $\beta=1$ was found. Addition of $R_2$ and $R_3$ contributions resulted in a diminished response exponent.

We recall that in our case the conductance of the three samples studied varied with CO concentration according to a power law with index, $\beta$, dependent on the pretreatment of the material: $0.1 (\text{for oxygen free decomposed samples}) < \beta < 0.5 (\text{for air decomposed sample})$. Since for the air decomposed sample the response exponent was larger than that for the oxygen free decomposed sample, the conductance in the later case must have been dominated by combination of $R_2$ and $R_3$ over $R_1$, resulting in lower measured gas response.
The proposed mechanism of room temperature CO sensitivity implies that electronic interaction between Pt additives and the support is essential, but the behavior is not specific to the choice of the semiconducting support. In this case the surface Pt serves as a receptor of the gas sensing action, which in turn is transduced into an electrical signal providing the electronic properties of the Pt control the transduction properties of the support. An obvious verification of the generality of the phenomenon would then be demonstration of the effect of gas sensitivity at room temperature for platinized semiconducting oxides other than SnO₂. This is undertaken in Chapter 6 of this work.
Chapter 4. Ru- Modified Tin Dioxide.

4.1 Experimental

4.1.1 Preparation

The route was through the preparation of a reactive Ru$^{2+}$ complex having only organic ligands, which would react readily with surface functional OH groups and from which the remaining ligands could easily be removed by pyrolysis.

*Reactive solution preparation:*

$(\eta^6$-$\text{C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}_4$ (supplied by D.A. Tocher, UCL, Chemistry) was mixed with AgBF$_4$ (1:5) and 10cm$^3$ of anhydrous acetone for one hour at room temperature. The solution was filtered through celite four times to remove the precipitate of AgCl. The orange solution of $[(\eta^6$-$\text{C}_6\text{H}_6)_3\text{Ru}($acetone$)_3]^{2+} (\text{BF}_4)_2$ (Ru precursor solution) was used in further preparations.

*SnO$_2$-0.2%Sb support pretreatment:*

To obtain reproducible initial conditions for the SnO$_2$-0.2%Sb support surface, the powder was first calcined at 400$^\circ$C under vacuum for 2 hours, and then oxidized at 400$^\circ$C for further 2 hours in pure oxygen (BOC). The material was then exposed to 100% relative humidity, by passing over it, overnight, an air stream (21%O$_2$ in 79%N$_2$, purity 99.99%, BOC) saturated with water at room temperature to rehydrate the surface. Finally to remove molecular water SnO$_2$-0.2%Sb was dried at 250$^\circ$C for 2 hours in vacuum.

*Grafting procedure:*

Powdered, preconditioned SnO$_2$-0.2at%Sb (200mg), was mixed into the bright orange Ru$^{2+}$ precursor solution (10cm$^3$) without exposure to ambient air, and stirred overnight at room temperature. Unreacted precursor solution was removed carefully by repeatedly subjecting the mixtures to centrifugal force, removing the solution and adding acetone. The final mixtures were filtered and the supported samples were pelletized under a force of 1000kg into 13mm diameter disks 1-2mm thick for study.
4.1.2 Supported materials pretreatment for gas sensitivity measurements.

As described in detail in section 2.2.2, measurements of the sample resistance response to trace gas concentrations and relative humidity in air were performed in the test rig. The pelletized samples for the resistance response measurements were mounted between gold electrodes inside a silica tube in a tube furnace. Prior to electrical resistance measurements the following pretreatments were performed.

**Pretreatment 1.** The Ru supported sample was reduced in 10%H\(_2\)/N\(_2\) mixture at 300\(^\circ\)C for 1 hour to decompose the Ru surface organometallic complex, and cooled down to room temperature under the above gas mixture. This pretreatment is called "reduction" throughout this report.

**Pretreatment 2.** The Ru supported sample was calcined in dry air at 300\(^\circ\)C for 1 hour to decompose the Ru surface organometallic complex and cooled down in dry air to room temperature. This pretreatment is called "decomposition in air" throughout this report.

*Repeated heating of the samples would alter the state of the surface and therefore a new "as prepared" sample was taken each time for a new set of measurements, wherever the decomposition stage was first applied.*
4.1.3 Materials characterization.

(i) UV-Visible spectroscopy.

Quantitative UV-Visible absorption measurements of solutions were used to estimate the amount of Ru reacted with the surface hydroxyl groups on SnO$_2$-0.2%Sb. The Bouquer-Lambert-Beer Law was employed:

$$A_\lambda = \varepsilon_\lambda \cdot c \cdot d$$

where $A_\lambda$ - specific adsorption, $c$ - concentration of the solution in mol l$^{-1}$, $\varepsilon_\lambda$ - molar decade extinction coefficient in l mol$^{-1}$ cm$^{-1}$ and $d$ - sample thickness in cm.

The original Ru(II) aryl acetone solution with $c_{Ru} = 1.8 \times 10^{-3}$ mol l$^{-1}$ was used as a standard to estimate the value of $\varepsilon_\lambda$ and the sample thickness was 1 cm. A typical UV-Visible absorption spectrum is given in Fig 4.1. The absorption peak at 394 nm for a Ru d-d transition is the only feature of the spectrum. $\varepsilon_\lambda$ (for $\lambda=394$) was estimated as 450 l mol$^{-1}$ cm$^{-1}$ which is within the typical range for d-d transitions [158].

![Figure 4.1 UV-Visible absorption spectra for the Ru precursor solution with $C_{Ru} = 1.8 \times 10^{-3}$ mol l$^{-1}$.](image)
For the blank measurement all stages of the grafting procedure were carried through, but without addition of the SnO$_2$-0.2\%Sb powder, to estimate the adventitious loss of Ru. 15cm$^3$ of the original Ru(II) precursor solution was stirred over night and filtered. The resultant solution was clear in this case, but in a real run it would contain residual SnO$_2$-0.2\%Sb powder, which would obstruct the adsorption measurements. The solution, therefore was further filtered through celite to mimic the necessary filtration step and the absorption spectrum collected.

The absorption spectrum of the Ru(II) acetone solution was then collected after the reaction with tin dioxide support and following its filtration. The amount of Ru, reacted with tin dioxide support was estimated as:

$$N_{\text{Ru}^{\text{SnO}_2-0.2\%Sb}} = N_{\text{Ru, blank}} - N_{\text{Ru, unreacted}},$$

where $N_{\text{Ru, blank}}$ is Ru concentration of the solution after the blank run and $N_{\text{Ru, unreacted}}$ is the Ru concentration of the solution after the reaction with tin dioxide.

(ii) Gas sensitivity measurements

Prior to gas sensitivity measurements, the pellets were pretreated in situ according to the two procedures described above.

The electrical resistance response to carbon monoxide and nitric oxide at room temperature was investigated in dry and moist air. Pellets thermally pretreated in situ were stabilized in dry air for 10 hours and then exposed to increasing concentrations (200, 400, 600, 800, 1000 ppm) of CO/NO in dry air with 1 hour at each concentration at room temperature. The atmosphere was then changed to moist air of 50\% relative humidity (RH) and the CO/NO test program repeated as above.
The required carbon monoxide concentration was obtained by mixing synthetic air (21% O\textsubscript{2} in 79%N\textsubscript{2}, purity 99.99%, BOC) with 1000 ppm CO in O\textsubscript{2} - N\textsubscript{2} (BOG) using mass-flow controllers (Tylan). The required nitric oxide concentration was obtained by dilution of pure NO (BOC) with synthetic air using manual flow controllers. Relative humidity in air was controlled by mixing dry air with air that had been saturated with water vapor by passing through a bubbler at room temperature (≈20\textdegree C). The total flow rate was 500 cm\textsuperscript{3} min\textsuperscript{-1}.

The electrical resistance response to carbon monoxide and nitric oxide at room temperature was also investigated in oxygen free atmosphere, using nitrogen as a background gas instead of air. Ru supported samples reduced \textit{in situ} were stabilized in dry nitrogen at room temperature for 10 hours and then exposed to increasing concentrations (400 and 800 ppm) of CO/NO in dry nitrogen with 1 hour at each concentration. This is referred to later as an "oxygen free" experiment. The required gas (CO/NO) concentration was obtained by dilution of the pure gases with nitrogen, using manual flow controllers.

(iii) X-ray photo electron spectroscopy

XPS analyses were first performed on the newly reduced sample. Subsequent XPS spectra were also taken after the sample was exposed to dry air only and after its exposure to air of 50% relative humidity. A sample decomposed in air was also examined. The object of the studies was to establish the surface composition of the sensors and in particular to verify the formation of a Ru surface complex and to determine the chemical state of Ru on the surface after subjecting the samples to different treatments. The sample preparation for each measurement was the same as for platinized SnO\textsubscript{2}-0.2%Sb (see Ch3) and a new "as prepared" sample was used.
The adventitious hydrocarbon C1s peak could not be used for satisfactory Fermi level referencing as the Ru 3d signal partially overlaps the C 1s signal. Therefore, the Sn 3d\textsubscript{s/2} peak was used as a binding energy reference and assigned a value of 486.7 eV [139]. No evidence for chemical shifts of the Sn 3d\textsubscript{s/2} was found since only one peak of constant FWHM (1.16± 0.05eV) was required to fit the region and the binding energy difference (ΔE\textsubscript{b}) between the O 1s and the Sn 3d\textsubscript{s/2} peaks was constant (ΔE\textsubscript{b} = 44.0 ± 0.1 eV) for all samples. However, C1s obstructions complicate both the determination of the exact Ru peak position and the quantification of the Ru peak areas. Thus a curve fitting procedure was applied in the Ru 3d region to enable separation of spectra into constituent peaks and therefore allow assignment. This, in the case of Ru 3d, was carried out by setting the 3d\textsubscript{s/2}:3d\textsubscript{3/2} peak ratio to 3:2 and the (3d\textsubscript{s/2}-3d\textsubscript{3/2}) binding energy difference to 4.1 eV [159]. RuO\textsubscript{2} was used as a standard and a binding energy of 282.5 eV was assigned to Ru(IV).

(iv) Temperature Programmed Desorption (TPD) and Temperature Programmed Decomposition (TPDE).

The methods have been described in Chapter 2. TPD studies in this case were performed under UHV conditions. TPDE/TPD spectra were recorded with a heating rate of 30°/min from room temperature to 350°C. TPDE spectra were recorded on initial heating of the samples to study decomposition of the Ru organometallic complex used to decorate the surface. The mass spectrometer signal for mass 78 (C\textsubscript{6}H\textsubscript{5}^+) was recorded with heating rate of 40°/min from room temperature to 450°C.

TPD of CO/NO was used to probe the distribution of Ru sites on the surface after decomposition of the Ru surface complex (removal of Ru organic ligands) at 350°C in vacuum. Decomposed samples were exposed to excess CO/NO (8x10^{-4} torr for 5 min) at room temperature, residual gas was pumped away and the base pressure of <10^{-8} torr was obtained prior to the start of the temperature ramp.
To study the oxidized surfaces the decomposed samples were first exposed to excess oxygen ($8 \times 10^{-6}$ torr for 5 min), followed by excess CO ($8 \times 10^{-6}$ torr for 5 min) at room temperature. A temperature ramp was performed after the evacuation to the base pressure of $<10^{-8}$ torr.

(vi) **Extended X-ray Absorption Fine Structure (EXAFS)**

EXAFS studies were performed on two Ru supported SnO$_2$-0.2%Sb samples one decomposed in air and one reduced. Both samples were subjected to ambient humidity before measurements. Analysis of the EXAFS region gives direct structural information in the form of bond distances, numbers and types of neighboring atoms.
4.2. Results.

4.2.1 Basic sample characterization: UV-Visible spectroscopy and electron probe microanalysis.

Table 4.1 summarizes the results of the quantitative uv-visible absorption measurements of the solution, performed to estimate the Ru sample loading. The data for the ruthenium aryl acetone solution after the blank experiment as well as for the solution extracted after the reaction with SnO$_2$-0.2%Sb are given.

Table 4.1 Ru content, N, for the ruthenium aryl acetone solution before and after reaction with SnO$_2$-0.2%Sb and for the blank run.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_{\text{Ru}}$/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>After blank run</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Remained unreacted</td>
<td>$1.3 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

The amount of Ru reacted with 200mg SnO$_2$-0.2%Sb support is therefore:

$$N_{\text{Ru}^\text{SnO}} = N_{\text{Ru, blank}} - N_{\text{Ru, unreact}} \approx 5 \times 10^{-6} \text{ mol} \approx 5 \times 10^{-4} \text{ g.}$$

Therefore the sample loading was 0.25 mass%. The surface area of the support was about $20 \times 10^4 \text{ cm}^2 \text{ g}^{-1}$ (see BET surface area measurements). Since 200 mg of the sample was used the total surface area was $4 \times 10^4 \text{ cm}^2$. The surface Ru coverage would then be $1.25 \times 10^{10} \text{ mol cm}^{-2}$. Combination of this information with XPS results to estimate the fraction of surface OH reacted with the Ru complex is given in the Discussion section of this chapter.
Electron probe microanalysis linescans were performed on a reduced sample to estimate the Ru distribution throughout the sample. The intensities for both Sn and Ru wavelength-dispersive X-rays signals were recorded simultaneously across the surface with 2\( \mu \)m steps and the results are presented in Fig. 4.2. Ru was found to be uniformly distributed over the sample within 2\( \mu \)m resolution.

![Graph showing Ru and Sn distributions](image)

**Figure 4.2** Electron probe microanalysis linescans of Ru and Sn with 2\( \mu \)m steps for the reduced SnO\(_2\)-0.2\%Sb- supported Ru sample
4.2.2 Gas-sensing properties.

The supported samples before decomposition of the Ru surface complex showed no CO room temperature resistance response.

(i) The resistance response to moisture, CO and NO in air.

CO response:

Plot of the resistance variation with CO concentration and relative humidity in air vs time for the reduced supported Ru sample given in Fig 4.3. Reduction of the supported Ru surface complex was performed in situ and was followed by the resistance measurements as an initial stage of an experiment. The data for an unmodified tin dioxide, similarly reduced (as per Fig.3.6) are also given in Fig 4.4. Note a slow dry air base-line resistance increase in the case of the Ru modified sample when dry air was applied for the very first time, following the sample reduction and cooling down to room temperature. This drift was not observed for the metal free sample, whose resistance instantly increased with the change of the reducing atmosphere to dry air and then remained stable.

A large resistance response to change of water vapor pressure in air was observed for both metal free and supported Ru sample. That is a well known characteristic of the n-type tin dioxide support. This effect is electronic rather than protonic and is attributed to a transformation from chemisorbed oxygen ions to hydroxyl groups as a dominant surface species [44,62]. In the case of the metal free sample the resistance simply recovered to the original value when dry air was reapplied. Note, however, a considerable upwards drift in the base line resistance in moist air for the Ru modified sample. On subsequent recovery in dry air the value for the base line resistance was increased, compared to that recorded in dry air prior to moisture exposure.
Metal-free material showed no room temperature resistance response to CO. The slight resistance variation observed initially in dry air was probably due to a slight variation in the water vapor pressure. In the case of the supported Ru sample a concentration dependent resistance response to CO was recorded in dry air on the very first exposure. Following the exposure to moisture the CO resistance response was reduced. This effect of moisture appeared to be irreversible. Thus, on subsequent measurements in dry air only a small resistance decrease with applied CO was observed.

Figure 4.3 Time profile of the room-temperature resistance of the reduced Ru modified SnO$_2$-0.2%Sb pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.
Figure 4.4 Time profile of the room-temperature resistance of the reduced SnO$_2$-0.2%Sb pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.

Response law:

Fig. 4.5 shows the resistance variation with CO concentration in dry air for the dry reduced sample. It can be seen that the sensor resistance is very sensitive to gas concentration. Double logarithmic plot illustration of the power law dependence of the resistance in dry air on CO concentration is given in Fig. 4.6. The dependence is assumed of a form: $\sigma = \sigma_0(1 + \kappa P_{\text{CO}}^\beta)$, where $\kappa$ is sensitivity and $\beta$ is the response exponent. From the above plot the response law was found to be of a form:

$$\Delta\sigma/\sigma_0 = 0.23 P_{\text{CO}}^{0.3}$$
Figure 4.5 Time profile of the room-temperature resistance of the dry reduced Ru modified SnO$_2$-0.2%Sb pellet as a function of exposure to ppm concentrations of CO in dry air.

Figure 4.6 Log-log plot of the room-temperature resistance response ($S = \Delta \sigma / \sigma_0$) versus CO concentration in dry air for the reduced Ru modified SnO$_2$-0.2%Sb.

Fig 4.7 shows the resistance variations with CO concentration and relative humidity in air for the Ru modified sample decomposed in air as a function of time. In contrast to the behavior of the reduced material no CO resistance response was observed. The behavior was the same as that of the unmodified support material treated in the same way Fig 4.8.
Figure 4.7 Time profile of the room-temperature resistance of the air decomposed Ru modified SnO$_2$-0.2%Sb pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.

Figure 4.8 Time profile of the room-temperature resistance of the air decomposed SnO$_2$-0.2%Sb pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.
Another Ru supported sample was again reduced \textit{in situ} and the effect of variation in NO concentration in dry air on its resistance is shown in Fig. 4.9. It can be seen that the reduced sample also showed a room temperature resistance response to NO in dry air. However, following removal of NO the resistance did not completely recover in dry air. Note again the base line resistance drift in dry air.

![Figure 4.9 Time profile of the room-temperature resistance of the dry reduced Ru modified SnO$_2$-0.2\%Sb pellet as a function of exposure to ppm concentrations of NO in dry air.](image)

Table 4.2. summarizes the values, $S$ for the resistance response of the dry reduced sample to 400ppm CO/NO in dry air. The values of the resistance response to the two test gases in air were similar and small.

<table>
<thead>
<tr>
<th>400ppm/dry air</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.68</td>
</tr>
<tr>
<td>NO</td>
<td>0.76</td>
</tr>
</tbody>
</table>
(ii) Resistance response to CO and NO in nitrogen—"air free experiment".

In the following experiment reduced Ru modified samples were not exposed to dry air directly after the reduction, but the gas sensing properties were first investigated in an oxygen free atmosphere. Reduction of a sample resulted in its resistance dropping to a few Ohms. To enable sensible measurements of the resistance response to be performed, samples for the air free experiment only were prepared using undoped SnO₂ as a support. All stages of the doping procedure were imitated with SnO₂ to produce a comparable support surface.

Figure 4.10 shows the resistance response to CO in nitrogen. Figure 4.11 shows the resistance response to NO in nitrogen. A decrease in the resistance of the reduced sample was observed on exposure to both CO and NO in nitrogen. Note, however that the resistance did not completely recover in nitrogen following an exposure to CO. Furthermore the resistance did not recover at all in nitrogen following an exposure to NO.

Table 4.3 summarizes the values, S for the sensor response to 400ppm CO/NO in nitrogen. It can be seen that the resistance response to both CO and NO of the newly reduced sample in "oxygen free" conditions was over 50% greater than the values measured in dry air.

<table>
<thead>
<tr>
<th>400ppm/in nitrogen</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2.33</td>
</tr>
<tr>
<td>NO</td>
<td>1.61</td>
</tr>
</tbody>
</table>
Figure 4.10 Time profile of the room-temperature resistance of the reduced Ru modified SnO$_2$-0.2\%Sb pellet as a function of exposure to ppm concentrations of CO in nitrogen in "air free experiment".

Figure 4.11 Time profile of the room-temperature resistance of the reduced Ru modified SnO$_2$-0.2\%Sb pellet as a function of exposure to ppm concentrations of NO in dry nitrogen in "air free experiment".
4.2.3 Detailed sample characterization.

4.2.3.1 Resistivity measurements in ambient air.

For comparison of the effects of the various treatments on the sample resistivity, measurements were made using a Wane-Kerr precision bridge, in a measurement cell which allowed a constant, manual force of 300kg to be applied to all samples. All samples were exposed to ambient air before measurements. The resistivities are summarized in Table 4.4 for the metal free sample as well as for the supported Ru sample after the reduction.

Table 4.4 Resistivities, \( \rho \), for SnO\(_2\)-0.2\%Sb and Ru\(^+\)SnO\(_2\)-0.2\%Sb after the reduction, exposed to ambient air.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>( \rho ) (reduced)/( \Omega ) mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO(_2)-0.2%Sb</td>
<td>3.78</td>
</tr>
<tr>
<td>Ru-modified</td>
<td>125.80</td>
</tr>
</tbody>
</table>

The effect of Ru surface grafting was to cause resistance increase. The supported Ru sample, following the reduction, showed an increased resistivity compared to the metal free tin dioxide reduced in similar way.

4.2.3.2 TPDE/TPD

Decomposition of the supported Ru complex on heating in vacuum gave a the signal for benzene evolution with maximum at around 230\(^\circ\)C as shown in fig. 4.12.

![Figure 4.12 Temperature programmed decomposition of the SnO\(_2\)-0.2\%Sb- supported Ru aryl complex: mass 78 (C\(_6\)H\(_6\)) signal.](image)
Following the decomposition of the Ru aryl complex in vacuum the Ru adsorption sites were probed with CO. Fig. 4.13 shows the multiple peak pattern in the TPD of CO for the supported Ru species after decomposition, recorded mass spectrometrically. TPD spectra of CO chemisorbed onto oxygen precovered Ru sites is shown in fig. 4.14. Signals for CO and CO\textsubscript{2} evolution were both observed in each case. At least three types of CO binding sites labeled A, B and C respectively were resolved whose proportion changed on oxidation.

![Figure 4.13](image1)

**Figure 4.13** Temperature programmed desorption spectra of ( ) CO and (—) CO\textsubscript{2} obtained after exposure of the reduced SnO\textsubscript{2}-0.2%Sb- supported Ru to excess CO (8x10\textsuperscript{4} torr for 5min) at room temperature. Heating rate 30° min\textsuperscript{-1}.

![Figure 4.14](image2)

**Figure 4.14** Temperature programmed desorption spectra of ( ) CO and (—) CO\textsubscript{2} obtained after exposure of the reduced SnO\textsubscript{2}-0.2%Sb- supported Ru to excess O\textsubscript{2} (8x10\textsuperscript{4} torr for 5min), following by excess CO (8x10\textsuperscript{4} torr for 5min) at room temperature. Heating rate 30° min\textsuperscript{-1}.
For the clean Ru sites (Fig 4.13 ) the three maxima are at 75, 150 and 270°C respectively, the 75°C peak “A” corresponding to the major binding state. The high temperature peak “C” is evidently due to the reaction between strongly chemisorbed CO and the lattice oxygen, resulting in CO₂ evolution.

For the oxygen precovered Ru sites again only CO evolution off site “A” was observed. However, the considerable loss in the intensity of low temperature CO desorption signal “A” seems to indicate that this CO adsorption site was largely or fully occupied by preadsorbed oxygen. The more tightly bound CO at site “B” showed a significant oxidation to CO₂ on desorption from the oxygen precovered Ru. Desorption from site “C” was again also associated with CO₂ evolution. A shift in the desorption temperature to a lower value (220°C) was recorded for the high temperature desorption peak “C”. The desorption temperatures remained unchanged for the peaks “A” and “B” for the case of oxygen precovered Ru sites.

Following the decomposition of a new batch of sample the Ru adsorption sites were probed with NO. The TPD spectrum for NO preadsorbed onto Ru sites after decomposition is shown in Fig. 4.15. It can be seen that NO preadsorbed onto the clean Ru sites appeared to desorb almost completely intact, signifying dominant non-dissociative adsorption. The spectrum of NO evolution shows two binding states. The two maxima occur at 125 and 300°C with the low temperature peak being the main binding state. Note that the main peak for NO evolution was recorded at a higher temperature compared to 75°C recorded for CO. This implies a stronger interaction of NO with supported Ru species.

A small signal of N₂ (mass 28) evolution was recorded, signifying some degree of dissociation of adsorbed NO. Klein and Shih [160] have demonstrated for the Ru metal surface that molecular nitrogen is only physisorbed, whereas nitrogen from NO decomposition is strongly chemisorbed and evolves with the main maximum at 237°C, which correlates well with the high temperature N₂ peak recorded here.
Figure 4.15 Temperature programmed desorption spectra of ( ) NO and (—) N₂ obtained after exposure of the reduced SnO₂-0.2%Sb- supported Ru to excess NO (8x10⁻⁴ torr for 5min) at room temperature. Heating rate 3⁰ min⁻¹.

To ascertain the CO (mass 28) interference from the vacuum background the blank temperature ramp was recorded, where the sample was simply left for half an hour in the UHV chamber at room temperature prior to measurements. Fig 4.16 shows the time profile of mass 28, recorded mass spectrometrically.

Figure 4.16 Blank TPD spectra recorded with 3⁰ min⁻¹ temperature ramp for the reduced SnO₂-0.2%Sb- supported Ru preexposed to vacuum background for 30min.
4.2.3.3 XPS studies.

(i) \( \text{SnO}_2 \)-0.2%Sb support

The O 1s X-ray photoemission signal for the unmodified support is given in Fig. 4.17. Two oxygen species were identified on \( \text{SnO}_2 \)-0.2%Sb surface with binding energies of 530.5 eV for the lattice oxygen contribution [139] and 531.8 eV for the hydroxyl group oxygen [161]. The peak at 530.8 eV is an Sb 3d_{5/2} signal due to the small amount of doping. Table 4.5 summarizes the qualitative contributions of the hydroxyl group and lattice oxygen to the total surface oxygen.

<table>
<thead>
<tr>
<th>oxygen species</th>
<th>(AT)/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice oxygen</td>
<td>76.4</td>
</tr>
<tr>
<td>hydroxyl</td>
<td>23.6</td>
</tr>
</tbody>
</table>

Table 4.5 \( \text{SnO}_2 \)-0.2%Sb surface oxygen constituents.

Figure 4.17 XP spectrum of the O 1s region for \( \text{SnO}_2 \)-0.2% Sb support pellet.
(ii) Undecomposed supported Ru aryl complex.

XP Ru 3d core level spectra for the original $\left\{ (\eta_6-C_6H_6)RuCl_2 \right\}_2$ precursor and the undecomposed supported Ru complex are shown in Fig. 4.18 & 4.19. C 1s obstruction at 284.8 eV (primarily due to the aryl ring) overlaps the $3d_{3/2}$ spin-orbit component of the Ru signal, but the lower energy Ru $3d_{5/2}$ component can be distinguished. An extra structure recorded in the carbon region for the supported sample is probably a consequence of acetone treatment. Shift to a higher binding energies was recorded for the $3d_{5/2}$ signal of the supported Ru. Note, however that the shape of the signal of the supported Ru is identical to that of the precursor and a narrow single peak is required in both cases to fit the region. Both species are defined by a single formal oxidation state.

Figure 4.18 XP spectrum of the Ru 3d region for $\left\{ (\eta_6-C_6H_6)RuCl_2 \right\}_2$ precursor.
Figure 4.19 XP spectra of the Ru 3d region for undecomposed SnO$_2$-0.2%Sb-anchored Ru aryl complex.

Table 4.6 summarizes peak positions and widths for the original dimer and the undecomposed supported Ru complex.

Table 4.6 Peak positions for \( \{ \eta^6-$C$_6$H$_6$)RuCl$_2 \}_2 \) and SnO$_2$-0.2%Sb-supported Ru complex as found by XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ru 3d$_{5/2}$ peak position /eV</th>
<th>Ru (3d$<em>{5/2}$-3d$</em>{3/2}$) energy difference/eV</th>
<th>Ru 3d$_{5/2}$ FWHM / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( { \eta^6-$C$_6$H$_6$)RuCl$_2 }_2 )</td>
<td>281.8</td>
<td>4.2</td>
<td>1.4</td>
</tr>
<tr>
<td>SnO$_2$ supported Ru</td>
<td>282.6</td>
<td>4.2</td>
<td>1.45</td>
</tr>
</tbody>
</table>

The binding energy for Ru 3d$_{5/2}$ core level of the surface complex species was 0.7eV greater than that for the precursor. The peak widths were the same for both samples.
(iii) Reduced Ru modified sample

*Ru 3d region:*

Fig. 4.20. shows the series of XP spectra in the Ru 3d core level region for the supported Ru complex, first directly after the reduction, then after subsequent exposure to dry air, finally after moist air. The peak positions for the Ru$^{2+}$ starting material and the bulk Ru metal are also given.

First of all note that the signal at 279.9eV characteristic for the bulk Ru metal [162] was not observed. After the reduction of Ru complex, the oxidation state of surface Ru species became very ill defined and could not be characterized by a single binding energy. There appeared to be at least three Ru surface species present with the lowest binding energy for the major state at 280.6 eV, which is 1.2eV lower than that recorded for the Ru$^{2+}$ of the precursor. After the exposure to dry air, a slight partial oxidation of the surface Ru took place, as shown by a positive binding energy shift for the Ru 3d$_{5/2}$ peak maximum.

![Figure 4.20](image-url)  
Figure 4.20 XP spectra of the Ru 3d region for SnO$_2$-0.2%Sb- supported Ru recorded following reduction (a), exposure to dry air (b), and subsequent exposure to air of 50% relative humidity (c).
The curve (a) in Fig 4.21 shows the difference between the two spectra normalized to C1s signal (maximum intensity of the C1s signal is taken as unity). There is a distinct peak (loss of species on air exposure) around 280.5eV and a broad drop (gain of species on air exposure) in the region of 281.5-283.0 eV. On subsequent exposure to 50% relative humidity in air, a further positive binding energy shift of the Ru3d₅/₂ peak maximum was recorded, characteristic of further oxidation of the surface Ru species. The spectrum is now characterized by a broad feature with maximum around 282.2 eV. Fig 4.21 curve (b) shows the difference spectrum normalized to C1s between the spectra of dry and wet air treated samples. This curve comprises of two peaks (loss of species on wet air exposure) with binding energies around 280.5eV and 281.2eV, and a drop (gain of species on wet air exposure) at 282.5eV.

Figure 4.21 XPS difference curves: (a) newly reduced sample - dry air treated sample and (b) dry air treated sample - wet air treated sample, for Ru modified SnO₂-0.2% Sb pellet. The spectra were normalized to C 1s signal.
The XPS data for the Ru surface content of the reduced supported Ru sample preconditioned in different environments are given in Table 4.7.

Table 4.7 Surface Ru content of SnO$_2$-supported Ru species before and after reduction, followed by dry and moist air exposures, as found by XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[\text{Ru}] / [\text{Sn+Ru+Sb}]%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-modified, undecomposed</td>
<td>2.82</td>
</tr>
<tr>
<td>Reduced in H$_2$N$_2$</td>
<td>2.41</td>
</tr>
<tr>
<td>Exposed to dry air</td>
<td>2.71</td>
</tr>
<tr>
<td>Exposed to moist air</td>
<td>2.53</td>
</tr>
</tbody>
</table>

The surface Ru content of all the samples remained unchanged.

**Valence band region:**

The X-ray excited photoemission spectrum within the valence band region for the reduced supported Ru sample after its exposure to ambient air is compared to that for metal free SnO$_2$-0.2%Sb in Fig 4.22. Note the formation of energy states within the SnO$_2$ band gap for Ru-modified sample and a slight broadening of a valence band edge towards the Fermi energy.

![Figure 4.22](image.png)

**Figure 4.22** XP valence band spectra of pure SnO$_2$-0.2%Sb (a) and Ru modified SnO$_2$-0.2%Sb (b).
Ru modified sample decomposed in air

Ru 3d-region:

Fig 4.23 shows a series of X-ray excited photoemission spectra in Ru 3d core level region for Ru modified SnO$_2$-0.2%Sb sample decomposed in dry air and subsequently exposed to 50% relative humidity in air. The spectrum of the sample decomposed in dry air appeared to be very similar to that observed for the reduced sample after its exposure to moisture. Surface Ru species are characterized by a broad feature in the XPS spectra with maximum around 282.2 eV. The peak intensity, however appeared to be considerably smaller than that observed for the reduced samples. On subsequent exposure to moist air (50% RH) no significant change in either peak position or intensity was observed.

Figure 4.23 XP spectra of the Ru 3d region for SnO$_2$-0.2%Sb- supported Ru recorded following decomposition in dry air (b), and subsequent exposure to air of 50% relative humidity (c).
The XPS data for the Ru surface content of the studied sample is given in Table 4.8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Ru]/[Sn+Ru+Sb]%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru modified, undecomposed</td>
<td>2.82</td>
</tr>
<tr>
<td>Decomposed in air</td>
<td>1.11</td>
</tr>
<tr>
<td>Exposed to moist air</td>
<td>1.42</td>
</tr>
</tbody>
</table>

The apparent surface Ru content of the air decomposed sample was decreased to half that before decomposition.

4.2.3.4 EXAFS.

Samples were subjected to prolonged exposure to ambient air prior to measurements.

(i) Reduced Ru modified sample

Fig. 4.24 (a) and (b) shows the Ru K-edge EXAFS oscillations for the reduced supported Ru species (after exposure to ambient air) and its Fourier transform, respectively. No metallic Ru-Ru bonding was found. The best curve fitting results were obtained based on a standard RuO$_2$ model as shown in Fig 4.25 (a). Only one peak corresponding to a shell of nearest neighbor Ru-O bonding was observed in the Fourier transform. No statistically significant second Ru—Ru shell could be modeled and no additional features could be seen in the Fourier transform above the background. This implies that we do not have a bulk RuO$_2$. 
Figure 4.24 Ru K-edge EXAFS spectra (a), and associated Fourier transform (b), of reduced Ru modified SnO$_2$-0.2%Sb. (---) Experimental spectrum, (—) theoretical best fit.
(ii) Ru modified sample decomposed in air.

Fig 4.25 (a) shows the EXAFS spectra for the supported Ru species after decomposition in air and exposure to moisture. Good fitting results were obtained on the basis of RuO$_2$ standard model. The intense peaks corresponding to the first Ru-O and second Ru--Ru bonding could be observed in the Fourier transform Fig. 4.25 (b). Evidently, bulk RuO$_2$ species were formed as a result of decomposition in air.

![EXAFS spectra and Fourier transform](image_url)

**Figure 4.25** Ru K-edge EXAFS spectra (a), and associated Fourier transform (b), of air decomposed Ru modified SnO$_2$-0.2%Sb. (___) Experimental spectrum, (---) theoretical best fit.
Table 4.9 summarizes the bond lengths, $r$, and coordination numbers, $N$, for the two studied samples, determined by EXAFS. The data for a RuO$_2$ standard are also given.

<table>
<thead>
<tr>
<th>Material</th>
<th>Atom type</th>
<th>$N$</th>
<th>$r$ / Å</th>
<th>$2\sigma^2$ / Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO$_2$</td>
<td>O</td>
<td>6</td>
<td>1.989</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>12</td>
<td>3.436</td>
<td>0.010</td>
</tr>
<tr>
<td>Ru$^{+}$SnO$_2$</td>
<td>O</td>
<td>4.3</td>
<td>2.047</td>
<td>0.008</td>
</tr>
<tr>
<td>reduced</td>
<td>Ru</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Ru$^{+}$SnO$_2$</td>
<td>O</td>
<td>6</td>
<td>1.925</td>
<td>0.006</td>
</tr>
<tr>
<td>air decomposed</td>
<td>Ru</td>
<td>2</td>
<td>3.079</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>3.515</td>
<td>0.008</td>
</tr>
</tbody>
</table>

It is apparent that the structure of the supported Ru species for the sample decomposed in air is that of RuO$_2$. Note however that the reduced Ru species as well as having only one nearest neighbor coordination, are characterized by lower coordination number and longer Ru-O bonding than the former, signifying a very small oxidized species.
4.3 Discussion

(i) Surface amount of Ru.

It is interesting to estimate the fraction of the SnO$_2$-0.2%Sb surface hydroxyl groups which reacted with the Ru complex. The SnO$_2$ (110) surface was used as a model for this purpose. The unit cell parameters were obtained from Camargo et al.[163] as $a = b = 4.5\AA$ and $c = 3.0\AA$. On this surface, if every exposed oxygen was hydroxylated, the number of surface hydroxyl groups would be $1 \times 10^{15}$ cm$^{-2}$. Assuming that three atomic layers were probed by XPS, a depth of about 10Å, the total number of lattice oxygen atoms probed by the measurement would be $6 \times 10^{15}$ cm$^{-2}$.

Therefore the surface hydroxyl contribution to the total oxygen signal would be about 14%, which is in fact slightly lower than that measured by XPS (23%). Therefore, given the approximation in the estimation, it is reasonable to assume a full surface hydroxylation.

The amount of Ru reacted with 200mg of SnO$_2$-0.2%Sb support was measured as $5 \times 10^{-6}$ mol or $30 \times 10^{17}$ atoms. The surface area of the support was about $20 \times 10^4$ cm$^2$ g$^{-1}$ (see BET surface area measurements) or $4 \times 10^4$ cm$^2$ per 200 mg. Thus, the surface loading of Ru was about $8 \times 10^{13}$ Ru atoms cm$^{-2}$, which means that about 10% of the total surface OH groups had reacted with the Ru complex.

We can also check the correspondence between XPS measurements and the estimate of Ru coverage obtained from the amount of complex reacted. So, the number of Sn atoms probed by XPS, based on the (110) model surface, would be $1 \times 10^{15}$ cm$^{-2}$ per layer. Assuming a measurement depth of three atomic layers implies $3 \times 10^{15}$ cm$^{-2}$. Based on the amount of complex reacted, the fraction of the total surface metal atoms which is Ru therefore would be about 3%, which is roughly the same as measured by XPS. Therefore, substantially all of the Ru atoms were visible to the XPS probe implying that none of the Ru was present in agglomerates more than about 3 atomic layers thick.
(ii) Surface state of the Ru and speculations on structure.

Surface bonded precursor

As a result of the reaction of Ru precursor complex $[(\eta_6-C_6H_6)Ru(acetone)_3]^2+$ with the hydroxyl groups of SnO$_2$-0.2%Sb, surface grafted Ru species were formed, characterized by a single oxidation state. From the literature survey [162,164,165] it is apparent that the straightforward assignment of the Ru oxidation state based on the XPS binding energy is highly complex and is largely dependent on the type of ligands, the conditions of the experiment, state of the surface, degree of hydration etc. However, as was demonstrated in detail by Citrin [166] it is possible to distinguish between Ru(II) and Ru(III) species, based on the XPS line width. He pointed out that the 3d level of the Ru(III) component is broadened by exchange splitting between the 3d and 4d electrons, while exchange splitting is absent for the case of the Ru(II).

We, however, did not detect any 3d peak broadening for the case of the supported Ru species prior to decomposition of the surface-bound precursor. The structure of the Ru 3d core level spectra for the supported complex was almost identical to that of the original dimer $[(\eta_6-C_6H_6)RuCl_2]_2$. Furthermore, the binding energy shift of 0.7eV recorded for the supported species is too small to suggest formation of the Ru(III) surface species. We also know from TPDE studies that the supported Ru retained the original aryl unit and that the grafted complex was rather stable, as its decomposition in vacuum took place only on heating to $230^\circ$C.

It is suggested therefore that the surface grafted Ru species remained in +2 oxidation state due to the formation of two direct Ru-O-Sn links, leaving the aryl unit intact. The binding energy shift would then be due to a substitution of the chlorines in the original dimer for more electronegative oxygens in the supported complex. The electronegativity of Cl is 3.0, compared to 3.5 for O [150].
Surface complex decomposed under \( H_2 \).

On the decomposition of the Ru surface bound complex under \( H_2 \) (reduction) we observed some degree of reduction of the Ru(II) species, recorded as a decrease in the XPS binding energy and a peak broadening. The signal characteristic of bulk Ru metal was not detected and therefore we suggest the formation of small surface bound unsaturated Ru clusters with varying nuclearity occurs.

It is suggested that such clusters of varying nuclearity appear in the XPS Ru 3d spectra as species with a broad range of formal oxidation states lower than 2+ but greater than zero. As only 10% of surface OH groups were used in Ru-O-Sn link formation and Ru was shown to be uniformly distributed over the surface those clusters would indeed be very small and the formation of monomeric surface bound species cannot be excluded. The assumption of monomeric surface-bound Ru allows interpretation of the TPD results for NO. This gas is known to adsorb mostly dissociatively onto Ru metal surfaces with only small amount desorbing as molecular nitric oxide [160]. A reasonable explanation for undissociated NO on the reduced supported Ru species is therefore that possibly two adjacent sites are required for dissociative adsorption. If, therefore, the Ru species anchored onto SnO\(_2\)-0.2%Sb, following the reduction of the surface complex, were close to monomeric, then NO could be chemisorbed in an undissociated state, which is what was observed.

Effect of ambient air on the reduced supported Ru.

Exposure to dry air caused a formal oxidation of the Ru species, and exposure to water vapor in air caused a further oxidation, as detected by XPS. The main oxidation state for the Ru surface species after water vapor exposure was recorded by XPS as similar to hydrated RuO\(_2\) \( \times \)H\(_2\)O [164]. Thus, on exposure to moisture in air of small surface clusters the cleavage of any Ru-Ru bond took place, resulting in the formation of hydrated surface bound Ru\(^{4+}\) centers.
Small oxidized Ru centers were revealed by EXAFS on the surface of the reduced sample, followed long exposure to air at normal ambient relative humidity. Peaks other than the nearest neighbor Ru-O were not observed and the coordination number was lower than that for bulk RuO₂. Thus those oxidized Ru species were obviously formed by oxidation of very small metal clusters or monomeric centers. Furthermore the Ru-O bond distance of 2.047 Å, measured by EXAFS, was longer than the Ru-O interatomic distance of 1.989 Å in bulk RuO₂. The EXAFS experiment gives averaged information on the local structure. For bulk RuO₂ on the surface, the metal-oxygen (support) interaction would be hidden by strong Ru-O interaction in an oxide particle. In our case, however, the cluster size appears small indeed, which would increase the proportion of the Ru atoms bound to the support oxygen. We believe that the measured elongated Ru-O bonding signifies the presence of chemical bonding between Ru species and the support oxygen. Comparison can be made with a number of EXAFS studies in the literature, reporting the interaction of the Ru metal clusters with various oxide supports. Lytle et al. [167] found a value of 2.18 Å for the interatomic distances between the Ru metal atoms and SiO₂ support oxygen. A value of 2.19 Å was reported by Asakura et al. [121] for the bonding between Ru and surface oxygen on TiO₂ support.

For the reduced Ru modified samples exposed to ambient air, XPS demonstrated that Ru forms energy states within tin dioxide band gap and causes slight broadening of the valence band edge. Furthermore the resistance in ambient air was shown to be higher than that for an unmodified sample, which is a direct evidence of an electronic interaction between Ru species and tin dioxide support, which could be expected on formation of Ru-O-Sn links to the surface.
Effect of decomposition in air.

The XPS spectrum of the supported Ru species formed after the decomposition of the surface complex in air was very similar to that recorded for the reduced moisture treated sample: that is, a formal oxidation state of Ru$^{4+}$. Furthermore, a lowering in the Ru surface content was found by XPS, signifying an agglomeration of the supported Ru. Formation of RuO$_2$ particles whose dimension was greater than the XPS probe depth would reduce the apparent Ru surface area observed by XPS and therefore the evaluated Ru concentration. Formation of RuO$_2$ particles was confirmed by EXAFS.

(iii) Electrical measurements and correlation with surface state.

On exposure of the in situ reduced sample to dry air, a positive base line resistance drift was recorded, characteristic only for the Ru modified sample. XPS studies of the reduced sample revealed partial oxidation of the surface grafted Ru on exposure to dry air recorded as a binding energy shift of the Ru 3d core level. The observed increase in the resistance in dry air is therefore a monitor of variation in the oxidation state of the surface Ru caused by oxygen adsorption. Oxidation of the supported Ru evidently was a time dependent process and therefore the resistance drift in dry air was rather gradual.

A further resistance increase was recorded in moist air. The XPS and EXAFS studies showed the formation of fully oxidized Ru$^{4+}$ centers after this treatment. Higher resistance values in dry air were recorded for the sample after its exposure to moist air. This can be interpreted as due to the formation of stable Ru species in +4 oxidation state. Ru(IV) lies deep in the band gap and is a very effective trap state, as is shown by its effect on electronic conductivity.
The gas sensitivity demonstrated for the newly reduced supported Ru samples in nitrogen is believed to arise directly from coordination of gaseous molecules with unsaturated surface bound Ru centers. We have demonstrated that both CO and NO indeed adsorb onto newly decomposed Ru species at room temperature. Three types of adsorbed CO species were identified, the species desorbing at 75°C being the major type. Desorption of NO was recorded at the higher temperature of 125°C. A resistance decrease was recorded on exposure to both CO and NO in nitrogen. In the case of NO the effect appeared to be completely irreversible: when pure nitrogen was reapplied no increase in the resistance was recorded. For the more weakly chemisorbed CO, however, a partial resistance recovery was observed in nitrogen.

Mizushima et al [168] studied CO adsorption onto Al₂O₃ supported Ru clusters by EXAFS and IR spectroscopy and found that the electronic state of the supported Ru was significantly perturbed on CO chemisorption. They observed three different CO adsorption bands in IR spectra and assigned those to linearly bound CO, and to symmetric and antisymmetric stretching vibrations of Ru-(CO)₂. They reported the average value for the Ru/CO ratio as 1.3, and demonstrated that the band due to the linearly bound CO disappeared on heating to 90°C. Following Mizushima et al [168] it seems that the linearly bound species were the major type of adsorbed CO species on SnO₂-0.2%Sb supported Ru in our study.

On the very first exposure of the reduced supported Ru sample to dry air the loss in gas sensitivity was over 50%. Evidently the reactive gas adsorption was obstructed by molecular oxygen. Chemisorption of molecular oxygen was confirmed by XPS, as a partial oxidation of surface Ru, and also by TPD studies, as an increase in CO₂ evolution.

We postulate that, at room temperature, the electronically active Ru site, responsible for the observed gas sensitive electrical conductivity, is the least strongly bound state labeled “A” in CO TPD. We propose that oxygen adsorption onto site “A” caused the observed resistance increase, and that CO substitution for oxygen caused the resistance decrease, measured as gas response. To support this interpretation, we recall that for oxygen precovered Ru species, the CO desorption signal “A” was significantly diminished,
signifying that CO substitution for oxygen is a chemically activated process. Interaction of the grafted Ru centers with moisture resulted in the formation of stable Ru$^{4+}$ hydrated species, thus blocking the CO adsorption site. Consistent with this observation, after exposure to moisture the sample gas sensitivity was lost irreversibly.

Decomposition in air of the surface bound complex resulted in the formation of bulk RuO$_2$ particles. In this case, the gas sensitivity of electrical conductivity was lost. The interpretation is that, in the bulk particles, the formal oxidation state of Ru was locked in Ru$^{4+}$ and the Ru was coordinatively saturated with tightly-bound oxygen, giving no means for gas adsorption to perturb the electronic states of the surface-attached particle. The behavior was that of the unmodified support material.

(iv) Summary and conclusion.

From the above discussion we believe that we have succeeded in surface grafting of the unsaturated Ru centers onto tin dioxide via a surface organometallic reaction and that the resultant modification of the electronic structure and electrical conductivity is also characteristic of the formation of chemical bonds. We demonstrated that the changes in electrical conductivity of the sample correspond to variation in the chemical state of the surface-bound Ru species caused by gas chemisorption. We showed that if the unsaturated surface centers are destroyed by thermal oxidation, the electrical effects are also destroyed.

5.1 Introduction

5.1.1 Objectives of this study.

DFT molecular cluster simulations were undertaken to probe the general qualitative trends in electronic structure modifications caused by Ru grafting and subsequent gas chemisorption onto supported Ru, with the aim of shedding light on the experimentally observed room temperature gas sensitive electrical behaviour from surface grafting of the Ru onto SnO₂-0.2%Sb. We did not attempt to calculate an actual electronic structure of the hydroxylated SnO₂-0.2%Sb surface, or reproduce quantitatively results obtained experimentally.

5.1.2 Stoichiometric hydroxylated SnO₂(110) surface

Tin dioxide crystallizes in the tetragonal rutile structure and the (110) surface is known to be the most stable when the material is stoichiometric [131]. A general view of the stoichiometric SnO₂ (110) surface is shown in Fig 5.1. A prominent feature of the surface is the rows of 'bridging ' oxygens which stand off the surface plane of Sn and O ions. The latter plane contains two kinds of Sn ions: exposed five-fold Sn ions (row A), and six-fold coordinated Sn ions (row B) lying beneath bridging oxygens. The O ions in plane are referred to as 'in-plane O'.
Bulk electronic structure calculations for SnO\textsubscript{2} [169] predicted a direct optical band gap of 3.6eV, in agreement with experimental results. According to Robertson [169] the conduction band minimum, which is about 4.5eV below the vacuum level (electron affinity), is 90\% Sn s-like state, and the valence-band maximum region, of 2eV width, consists mainly of oxygen p lone-pair orbitals. Recent DFT-pseudopotential calculations of Manassidis \textit{et al} [132], simulating the SnO\textsubscript{2} (110) stoichiometric surface by periodic three dimensional slabs separated by vacuum layers, demonstrated that for stoichiometric SnO\textsubscript{2}(110) surface the states at the valence band maximum are O p-like and strongly localized on bridging oxygens, with some weight also on sub-bridging oxygens. Only moderate atomic relaxations for the stoichiometric (110) surface were found, being on the order of 0.1-0.3Å. Five-fold coordinated Sn was found to move into the surface, while in-plane O and six-fold coordinated Sn were found to move out. The experimental evidence shows that on the stoichiometric surface there are no states in the gap [170].

Figure 5.1 Perspective view of the stoichiometric SnO\textsubscript{2}(110) surface and a part of the bulk in (110) direction, small and large spheres represent Sn and O respectively.
In this work we are concerned with the hydroxylated SnO$_2$(110) surface, since anchoring of the Ru organometallic complex onto SnO$_2$ surface proceeds via surface hydroxyls. Recent TDS and UPS studies by Gercher and Cos [171] show the presence of dissociatively adsorbed water on SnO$_2$(110) at 300K. It is believed that the dissociative configuration has the water OH$^-$ ion at the five-fold site (a terminal hydroxyl), and the H$^+$ ion attached to a bridging O ion to form a second type of hydroxyl ion (a bridging hydroxyl) [43,62]. The DFT-pseudopotential calculations of Goniakowsky and Gillan [131] on the fully hydroxylated SnO$_2$(110) surface in slab geometry with periodic boundary conditions, show that in the relaxed configuration the bridging oxygen and the adsorbed terminal hydroxyl group oxygen (O$_A$) approach each other, and the proton attached to bridging oxygen tilts towards O$_A$ to form a hydrogen bond of 1.81Å. The calculated total density of states and local density of states for the two hydrated oxygen sites showed that the contribution due to the bridging oxygen atom, situated at the top of the valence band for clean surfaces, was pushed towards lower energies. The adsorbed hydroxyl group was shown to give a contribution to the valence O2p band, which was at the surface valence band maximum. No states in the gap were reported.

5.1.3 Molecular models approach.

An ideal tin dioxide surface can be considered as being composed of a regular three dimensional arrangements of atoms repeated infinitely in two dimensions. As was already mentioned, the solid-state physics approach to model the properties of surfaces is to start from the idea of a periodic solid simulated by a semi-infinite slab, and exploit the translational symmetry of a crystal [126]. In the 'molecular' approach the structure of the site of interest is replaced by finite models such as real or hypothetical molecules that can be treated by the same first principles methods applied to molecules [172]. Hence the problem of electronic structure and local geometry of the solid is reduced to the common problem of determining the geometry and electronic structure of molecules, where the explicit treatment is confined to the atoms and interactions of significance for the effect under study.
Hence in the molecular approach the electronic structure of bulk oxide, characterized by energy bands separated by a band gap, is represented by a discrete set of bonding and antibonding molecular orbitals [173], where the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are separated by a HOMO-LUMO gap (Fig 5.2).

One of the consequences of long range periodicity within a three dimensional crystal lattice is that the local atomic and electronic structure will be influenced by more distant atoms in the surface plane and by atoms within the bulk of the lattice. The main limitation of the calculations on the small clusters is that they are not sufficient for the correct description of the electronic field created around the constituent atoms in the bulk. Thus any analogy between molecular models and the properties of solid surfaces is limited, since any collective electronic and structural characteristics of the crystal lattice may have no counterparts among molecular models containing relatively few atoms. In spite of limitations, however, the molecular approach has been successfully employed to tackle local phenomena, i.e. to describe active surface sites [124,127-129] or adsorbate on the surface [129,133,174] as well as supported surface systems [134,175] because it is believed that the localized electronic states are scarcely affected by limited cluster sizes [124,172].
Rantala et al [174] reported an ab initio molecular cluster approach to simulation of local electronic structure variations of SnO$_2$(110) induced due to surface oxygen vacancies, Cr impurity atom and NO adsorption. A cluster model of up to 100 atoms was proposed to be able to reflect the energy levels of the surface. Band-gap levels were found to arise from bridging oxygen vacancies at SnO$_2$(110) surface in agreement with experimental findings. Chromium surface impurities were found to create deep trap levels at the bottom of the band gap and were proposed to result in an increase in surface band bending, explaining the large drop in the electrical conductivity of Cr$_2$O$_3$ doped SnO$_2$. Adsorption of NO onto the Cr surface impurity was found to proceed by transfer of an extra electron from surface Cr to the antibonding $2\pi^*$ orbital of NO. It was proposed that the latter may weaken the N-O bond, which may explain the enhanced adsorption and dissociation of NO on SnO$_2$ surfaces having chromium impurities.

5.1.4 Cluster embedding.

In constructing molecular models, cutouts from the surface are made, representing the sites of interest, and are treated like molecules. The electronic properties of a point defect or an adsorbate on the surface are often determined by the local environment and require a localized description [172]. On the other hand, it is essential to take into account solid-state effects by “embedding” the local cluster model in the host crystal.

When cutouts are made from oxide solids with largely covalent bonds, the ‘dangling’ bonds that would connect the chosen site with the bulk of an oxide are commonly saturated by hydrogen to yield hypothetical or real molecules as models [128,176,177]. This is a very simplified approach, however, and more rigorous embedding techniques represent the bulk of the oxide crystal, surrounding the explicitly treated cluster model by a finite array of point charges located at the atoms or ions at the bulklike positions [134,172,176]. Depending on the ionicity of an oxide the formal charges of the point ions are adjusted to give a close representation of the long-range Madelung potential; in the case of partially
covalent solids fractional charges are needed. The idea of terminating the cluster by real
atoms (hydrogen), however, gained popularity because it is in line with chemists' intuition
and the computer programs are readily available for molecular orbital calculations. In
general, for largely covalent materials this has been shown to be a reliable approach
[128,176,178]. In the present work the SnO$_2$ surface sites are modeled by hydrogen
saturated clusters.

Rittner et al [178] reported *ab initio* cluster calculations for adsorption of nitrogen on
TiO$_2$ (110) surface, employing Hartree-Fock self-consistent field (HF SCF) methods. A
Ti$_9$O$_{23}$ cluster was used to represent the surface adsorption site, where full nearest
neighbours coordination was included for the central Ti atom and each adjacent oxygen
atom. The cluster model was either embedded in a point charge array or the terminating
oxygen atoms were saturated by hydrogen atoms. The point charges were varied between
+1.0 to +4.0 for Ti (-0.5 to -2.0 for O). In addition, in some calculations the cores of the
cations directly adjacent to the O atoms of the cluster were simulated by effective core
potentials (ECP). Rittner et al [178] showed that hydrogen saturation of the clusters was
not inferior to the more sophisticated embedding scheme using Madelung fields of point
charges. In fact they showed that for a fixed cluster size the saturation by protons simulated
an environment which seemed more realistic than an embedding in pure point charges or
point charges plus ECP's; the hydrogen saturated cluster offered a better representation of
the electronic structure at the coordinately unsaturated Ti adsorption site. Hence the N$_2$
end-on adsorption energy estimated with the cluster embedded in a point charge array was
46 kJ/mol, which was considered to be too high. The value of 37kJ/mol obtained with the
hydrogen saturated cluster was taken to be a more reliable estimate, close to the
experimental value of 34-36kJ/mol.
5.1.5 Techniques of density functional theory

Density functional theory, developed by Hohenberg and Kohn [179] and Kohn and Sham [180] allows one, in principle, to map exactly the problem of a strongly interacting electron gas (in the presence of nuclei) onto that of a single particle moving in an effective modified external field. The main approximation to the theory is in fact that this effective potential is not known precisely.

Hohenberg and Kohn proved that the energy of a many-electron system is a unique functional of electron density, \( \rho(r) \). Hence, to get the energy one need not know the many-particle wave function \( \Psi(r_1, r_2, ..., r_n) \), but the one-particle density only, which is a function of only three coordinates. The minimum value of the total energy functional is the ground-state energy of the system, and the density that yields this minimum value is the exact single-particle ground state density. Kohn and Sham have further shown how it is possible to replace the many-electron problem by an exactly equivalent set of self-consistent one-electron equations. Only the minimum value of the total energy functional has physical meaning and the density that yields the minimum energy of a given system can be found by solving the Kohn-Sham one-electron equations:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ne}}(r) + e^2 \rho(r')/|\mathbf{r} - \mathbf{r}'| \, d^3r' + V_{\text{XC}}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r)
\]  

(5.1)

where \( \psi_i(r) \) is a wave function of electronic state \( i \), \( \varepsilon_i \) is the Kohn-Sham eigenvalue, \( V_{\text{ne}}(r) \) is the total nuclear/electron attraction potential, and the term \( V_{\text{XC}}(r) \) is called the exchange-correlation potential. \( V_{\text{XC}} \) is defined to be the functional derivative:

\[
V_{\text{XC}}(r) = \delta E_{\text{XC}}[\rho(r)] / \delta \rho(r),
\]

(5.2)

where \( E_{\text{XC}} \) is the exchange-correlation energy.
Note that the charge density of a system for which we know the \( \psi \), is given simply by:

\[
\rho(r) = \sum |\psi(r)|^2
\]  

(5.3)

The one-electron eigenstates, \( \psi_i(r) \), can be treated in a familiar LCAO expansion:

\[
\psi_i(r) = \sum \alpha_k \chi_{ik}
\]

(5.4)

with atomic orbitals, \( \chi_{ik} \), basis set in a form of, for example, Slater-type atomic orbitals.

If the exchange-correlation energy functional were known exactly, the Kohn-Sham equations could be used to determine the exact charge distribution and wavefunction of any electronic system of interest. The major issue in DFT is the approximation used for \( E_{XC} \).

The total electron-nucleus interaction potential, \( V_{ne}(r) \) (eqn. 5.1), for a given charge density and nuclear potential field at \( r \) is given by:

\[
V_{ne}(r) = \int \rho(r) v(r) d^3r
\]

(5.5)

The Kohn-Sham equations must be solved self-consistently so that the occupied electronic states generate a charge density that produces the \( V_{ne} \) potential that was used to construct the equations.

The Kohn-Sham equations (5.1) are a set of eigenequations, and the terms within the brackets can be regarded as a Hamiltonian where

\[
V_{ne}(r) + e^2 \int \rho(r') |r - r'| d^3r' + V_{XC}(r) = V_{eff}(r)
\]

(5.6)

is Kohn-Sham effective potential, and the Kohn-Sham equations (5.1) represent mapping of the interacting many-electron system onto a system of noninteracting electrons moving in an effective modified external potential.
The simplest method of describing the exchange-correlation energy of an electronic system is to use the local density approximation (LDA) \([125,136]\) and most DFT work on solids is based on this approximation \([130,136]\). In LDA the exchange-correlation energy of an electronic system is constructed by assuming that the exchange-correlation energy per electron at a point \(r\) in the electron gas, \(\varepsilon_{xc}(r)\), is equal to the exchange-correlation energy per electron in a homogeneous electron gas that has the same density as the electron gas at point \(r\). Then

\[
E_{xc}[\rho(r)] = \int \varepsilon_{xc}(r) \rho(r) d^3 r
\]

(5.7)

where \(\varepsilon_{xc}(r) = \varepsilon_{xc}^{hom} [\rho(r)]\)

To obtain \(E_{xc}[\rho(r)]\) only the value of \(\rho(r)\) at \(r\) is needed and hence the exchange-correlation energy is purely local. Several forms exist for the exchange-correlation energy of a homogeneous electron gas all of which lead to total energy results that are very similar \([125]\). In this work the LDA calculations were performed using the parametrization of the homogeneous electron gas density given by Vosko, Wilk and Nusair \([181]\).

Attempts to improve density functionals are based on including non-local corrections to account for inhomogeneity of the electron density in the real \(n\) electron system. A number of nonlocal density corrections have been developed in which the \(E_{xc}[\rho(r)]\) is evaluated not from the local value of the electron density but also from the gradient of \(\rho(r)\) at \(r\) \([136,182]\). The approach is known as the generalized gradient approximation (GGA). It has been shown that these corrections lead to improvement in the calculation of total energies of atoms and molecules \([181]\). In this work the popular GGA scheme due to Becke \([183]\) and Perdew \([184-]\) is employed.
5.2 Methods

5.2.1 Build up of molecular models.

SnO$_2$ has a rutile crystal structure [185] which is 6:3 coordinated, and a six-atom rutile unit cell is shown in Fig. 5.3. In the bulk each Sn atom is surrounded by six oxygen atoms and each oxygen is surrounded by three Sn atoms. The atom coordinates are Sn: (0,0,0), (1/2,1/2,1/2) and O: +(x,x,0), +(1/2+x,1/2-x,1/2). In this study polycrystalline SnO$_2$ was used with particle size around 50nm (Fig 2.7, 2.8). Rutile of this dispersion is believed to expose predominantly (60-85%) the thermodynamically most stable (110) crystal plane [178]. It is therefore reasonable to model the SnO$_2$ support surface as a (110) model surface. We have assumed further a full hydroxylation of the (110) surface in agreement with our experimental results (Chapter 4). The shaded area in Fig 5.3 represents the (110) crystallographic plane. An extended structure of SnO$_2$(110) crystal plane without any reconstruction and a part of a bulk structure in (110) direction was given in Fig. 5.1.

![Figure 5.3 The unit cell of the rutile crystal structure drawn so as to emphasize the octahedral metal-oxygen coordination.](image-url)
The stoichiometric hydroxylated SnO$_2$(110) surface was modeled with molecular clusters of increasing size Sn$_n$O$_m$H$_x$. Clusters were constructed based on geometrical parameters for the bulk SnO$_2$. Geometrical parameters were obtained from Camargo et al.[163] for the optimized structure: $a = b = 4.478\AA$, $c = 3.009\AA$ and the internal parameter $x = 0.003\AA$. As in the bulk SnO$_2$, a stoichiometric cluster model should have 2:1 O-to-Sn ratio. In the case of a non-stoichiometric cluster an electronic charge must be added to compensate for the missing neighbours. The number of electrons in the cluster models is determined based on the assumption that Sn, O and H have formal charges of +4, -2 and +1, respectively. The dangling bonds of peripheral oxygen atoms of the cluster were electronically saturated by hydrogen atoms. The initial distance $R$(O-H) was chosen to be 0.970Å and the protons were placed along the O-Sn direction. The chosen scheme of cluster embedding was to reoptimize the positions of saturating hydrogen atoms to equilibrium. Hence in every set of calculations reported in this section optimisation of the positions of hydrogen atoms is assumed. More detailed description of the particulars of each set of calculations and the cluster geometry is given in the text.

5.2.2 Computational.

The electronic structure calculations were performed within the density functional theory, by using mainly the local density approximation (LDA) and in some cases the Becke and Perdew [183,184] generalized gradient approximation scheme (GGA) for the exchange and correlation energy. The calculations have been performed using the Amsterdam Density Functional (ADF) code [186], running on an Indigo-2 Silicon Graphics workstation, and on the Columbus central computing facility. Within the code Kohn-Sham one-electron molecular orbitals are represented by linear combinations of atomic orbitals (LCAOs) using basis sets of Slater type orbitals. LCAO allows projection of the electronic levels of the molecular cluster model onto the atomic orbitals. The determination of the ground state is performed by minimizing the total energy of the system with respect to the Molecular Orbital coefficients. All geometry optimizations are performed by computing analytical gradients of the total energy.
The basis orbitals were constructed using the commonly employed frozen core approach, where it is assumed that the core orbitals have exactly the same form as in free atoms. Hence only valence electrons are represented explicitly in the calculations, the valence-core interactions being represented by effective core potentials (ECP) which are generated by DFT calculations on free atoms. For the Sn atoms all electrons up to and including the 4p shell are treated as part of the core, so that there are fourteen explicitly treated electrons (4d^{10}5s^25p^2 in the neutral atom), while for Ru the core consists of electrons up to 3d, with 16 electrons (4s^2 4p^64d^75s^1 in the neutral atom) counting as valence electrons. For O the core consists of the 1s shell, so that there are six electrons (2s^22p^4 in the neutral atom) treated explicitly, similarly to C where the 2s and 2p levels were treated as the valence shell and the 1s level as the core shell. Basis sets of Slater type orbitals of double zeta (DZ) quality have been used throughout, which in some cases were extended to triple zeta plus polarization (TZP) quality (polarization functions were used only for the O atom). The particulars are given in the text.
5.3 Results

5.3.1 Unmodified surface models.

The hydroxylated SnO₂ (110) surface was modeled by clusters of increasing size (Fig 5.4). All clusters were constrained to $C_{2v}$ symmetry. The smallest cluster used was $[\text{Sn}_n\text{O}_m\text{H}_p]^z$, which represents a "2-fold" tin dioxide adsorption site, consisting of two row A tin atoms (see Fig 5.1) and a full nearest-neighbor coordination cell of 5 lattice oxygens and one terminal OH group for each Sn atom. To emphasize that the oxygen atoms directly above the five-fold lattice oxygen coordinated tin atoms are those of the surface hydroxyl groups, the corresponding Sn-O bond distance was reduced by 5% [131] as compared to the bulk Sn-O bond distance, and was not fixed. The positions of those oxygen atoms were optimized by energy minimization within the constraints of $C_{2v}$ symmetry, whereas all other heavy atoms were fixed as in a bulk SnO₂.

In the next $[\text{Sn}_q\text{O}_r\text{H}_s]^z$ cluster model two more row A tin atoms and corresponding oxygen atoms and terminal OH groups were added. Finally the cluster was further extended to $[\text{Sn}_t\text{O}_u\text{H}_v]^z$ to contain row-B Sn atoms and the full oxygen coordination around each added tin atom was maintained; the subbridging oxygens and bridging hydroxyls were therefore included in this cluster. The positions of the oxygen atoms above the 5-fold lattice oxygen coordinated Sn were not fixed to allow optimization as they represented the terminal hydroxyl group oxygens, but the other heavy atoms were fixed at the positions of a bulk SnO₂ (including oxygens of the bridging hydroxyls). It should be noted that, as described in section 5.2.1, the positions of all hydrogen atoms were optimized within the constraints of $C_{2v}$ symmetry in every set of calculations reported here.
Figure 5.4 Hydrogen saturated molecular cluster models for stoichiometric hydroxylated SnO$_2$(110): Large spheres - Sn, medium spheres - O, and small spheres - H.

(a) [Sn$_2$O$_{16}$H$_{10}$]$^{2-}$

(b) [Sn$_4$O$_{18}$H$_{18}$]$^{2-}$
(c) [Sn₉O₆H₃₆]⁺
(i) LDA calculations on unreconstructed clusters of increasing size.

In the first series of calculations the local density approximation (LDA) was used, the surface relaxation was not considered, and basis sets of double-zeta quality were used for all atoms. The computed LDA energy levels for the three clusters are shown in Fig. 5.5. We concentrate only on the electronic structure and the origin of the cluster levels around the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals.

![Figure 5.5 LDA MO diagrams around the HOMO-LUMO gap, indicated by arrows, of (a) [Sn$_{2}$O$_{10}$H$_{10}$]$^{2-}$, (b) [Sn$_{4}$O$_{18}$H$_{18}$]$^{2-}$, and (c) [Sn$_{10}$O$_{40}$H$_{34}$]$^{4-}$ molecular clusters.](image)

Table 5.1 summarizes the atomic compositions of the energy levels around the HOMO-LUMO gap.

Table 5.1. LDA eigenvalues and atomic compositions for the energy levels around the “band gap” for \([\text{Sn}_2\text{O}_{10}\text{H}_{10}]^{2-}\), \([\text{Sn}_4\text{O}_{18}\text{H}_{18}]^{2-}\) and \([\text{Sn}_{10}\text{O}_{40}\text{H}_{54}]^{2-}\) clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>orbital</th>
<th>Energy/eV</th>
<th>Composition/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Sn}<em>2\text{O}</em>{10}\text{H}_{10}]^{2-})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9a_2</td>
<td></td>
<td>3.117</td>
<td>650^2p, 22O^2p, 10O^2p</td>
</tr>
<tr>
<td>14b_2 (HOMO)</td>
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<td>3.437</td>
<td>83O^2p, 9O^2p</td>
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<tr>
<td>17a_1 (LUMO)</td>
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<td>5.453</td>
<td>62H^13, 24H^13</td>
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<tr>
<td>12b_1</td>
<td></td>
<td>6.449</td>
<td>50H^19, 27Sn^1, 15H^13</td>
</tr>
<tr>
<td>([\text{Sn}<em>4\text{O}</em>{18}\text{H}_{18}]^{2-})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19b_1</td>
<td></td>
<td>0.908</td>
<td>44O^2p, 29O^2p, 26O^2p</td>
</tr>
<tr>
<td>17a_2 (HOMO)</td>
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<td>0.909</td>
<td>44O^2p, 30O^2p, 25O^2p</td>
</tr>
<tr>
<td>30a_1 (LUMO)</td>
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<td>28b_2</td>
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<td>3.688</td>
<td>74H^33, 10H^23</td>
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<td>([\text{Sn}<em>{10}\text{O}</em>{40}\text{H}_{54}]^{2-})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50b_1</td>
<td></td>
<td>10.449</td>
<td>82O^2p, 33O^2p, 8O^2p</td>
</tr>
<tr>
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<td></td>
<td>10.45</td>
<td>82O^2p, 33O^2p, 8O^2p</td>
</tr>
<tr>
<td>61a_1 (LUMO)</td>
<td></td>
<td>11.62</td>
<td>31H^77, 30H^73, 6Sn^3</td>
</tr>
<tr>
<td>51b_1</td>
<td></td>
<td>12.28</td>
<td>27H^77, 19H^73, 7H^65, 6Sn^3, 5H^57</td>
</tr>
</tbody>
</table>

\(C_{2v}\) symmetry notation is used to label the orbitals. The number superscripts at the atomic symbols correspond to their location in the cluster from Fig 5.4. Each superscript implies all atomic species connected by \(C_{2v}\) symmetry.

The highest occupied levels in all clusters are of oxygen 2p character and we refer to those as “valence” orbitals for the sake of argument. In Fig. 5.5 we have identified the LUMO in each case as the bottom of the assumed “conduction” orbitals. The conduction orbitals are of mixed tin-hydrogen origin, which we believe to be the inevitable result of the limitations of the present calculations: limited cluster size with the end oxygen atoms saturated by protons. We should point out, that the aim of the calculations in this section was to identify the general qualitative features characteristic for unmodified clusters, studied here, so that the effects of the attached Ru could be ascertained.

The “band gap” width was calculated to be about 2eV for the two clusters containing only row A tin atoms (2.02 and 1.91eV) and 1.17eV for the cluster where row B tin atoms were included.
(ii) GGC calculations on fully relaxed $[\text{Sn}_2\text{O}_{10}\text{H}_{10}]^{2-}$ cluster.

In the second series of calculations we consider qualitatively the effect of the addition of non-local density corrections (generalized gradient correction GGC) to LDA on the evaluated electronic structure. In addition, the basis sets were improved to triple-zeta quality for all atoms and the positions of all heavy atoms were optimized by energy minimization within the constrains of $C_2v$ symmetry. The calculations were done on the smallest cluster $[\text{Sn}_2\text{O}_{10}\text{H}_{10}]^{2-}$.

GGC electronic structure around the HOMO-LUMO gap of the $[\text{Sn}_2\text{O}_{10}\text{H}_{10}]^{2-}$ cluster with the positions of all heavy atoms relaxed to equilibrium is depicted in Fig 5.6. Table 5.2 summarizes the composition of those orbitals around the "band gap".

![Diagram](image)

Figure 5.6 Generalised gradient corrected MO diagram around the HOMO-LUMO gap, indicated by arrows, of $[\text{Sn}_2\text{O}_{10}\text{H}_{10}]^{2-}$ molecular cluster of relaxed geometry.
Table 5.2 GGC eigenvalues and atomic compositions for the energy levels around the "band gap" for \([\text{Sn}_2\text{O}_{10}\text{H}_{10}]^2\) clusters.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy/eV</th>
<th>Composition/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a_2</td>
<td>0.999</td>
<td>91O_2^3</td>
</tr>
<tr>
<td>11b_2 (HOMO)</td>
<td>1.005</td>
<td>77O_2^3, 11O_2^9, 6O_2^5</td>
</tr>
<tr>
<td>17a_1 (LUMO)</td>
<td>4.897</td>
<td>27H^{13}, 25H^{13}, 25H^{21}, 13H^{19}, 9Sn^{51}</td>
</tr>
<tr>
<td>15b_1</td>
<td>5.779</td>
<td>46Sn_{2p}^{4}, 38H^{13}, 14H^{19}</td>
</tr>
</tbody>
</table>

C_{2v} symmetry notation is used to label the orbitals. The number superscripts at the atomic symbols correspond to their location in the cluster from Fig 5.4. Each superscript implies all atomic species connected by C_{2v} symmetry.

The "valence" orbitals are constructed with O 2p levels and the "conduction" orbitals are composed of mixed tin-hydrogen levels. The HOMO-LUMO band gap width was evaluated to be 3.9eV for the gradient corrected calculations on the relaxed cluster.

It should be noted here that Density Functional Theory (independent of the choice of exchange-correlation energy functional) is, in principle, not designed to yield correct band gaps, as was demonstrated in detail by Godby, Schluter and Sham [136]. They showed that reduced energy gaps in semiconductors and insulators are usual for DFT eigenvalues. However, they also pointed out that the discrepancy varies for different systems and in some cases DFT gives more accurate band gaps than in the others. They suggested that when the differences between the experimental and the DFT band gap widths are not great, improvements of up to 20% in the values obtained with LDA are expected by going beyond the local density approximation.

Evidently, great care should be taken in interpretation of DFT band gaps, as the evaluation of correct energy gaps within DFT is complicated and beyond the scope of this work. We have, however, by gradient corrected calculations on the relaxed \([\text{Sn}_2\text{O}_{10}\text{H}_{10}]^2\) cluster, obtained the band gap width of 3.9eV, which is very close to the experimental value of 3.6eV. This lends credibility to our calculations, but we feel that it is dangerous to rely on the results for the band gap widths and draw any conclusions from the variations in the obtained values concerning electrical behaviour of the material. In this discussion we therefore discard any quantitative characteristics of band gaps and concentrate on qualitative modifications in electronic structure caused by Ru grafting.
Apart from the value of the band gap itself, the general features of electronic structure around the HOMO-LUMO gap, obtained in gradient corrected calculations, appear to be qualitatively very similar to that obtained with LDA.

Before moving to the last calculations in this section we should note that so far we have only considered the stoichiometric hydroxylated SnO\(_2\) surface, whereas in practice SnO\(_2\)-0.2\%Sb was used as a support. The latter exhibits extrinsic electrical conductivity at room temperature owing to the fact that excess electrons due to the pentavalent dopant are forced to occupy energy states just below the bottom of the conduction band.

In the following calculations we imitated extrinsic electrical behaviour of the studied clusters by introducing an extra charge. The GGC calculations were performed on [Sn\(_2\)O\(_{10}\)H\(_{10}\)]\(^{3-}\) (note the -3 charge) cluster using extended triple-zeta basis sets for all atoms and allowing full cluster geometry relaxation within the constraints of C\(_{2v}\) symmetry. Fig 5.7 shows the calculated orbital diagram. Two full circles indicate the highest fully occupied MO, which is constructed with O 2p levels; this molecular orbital corresponds to HOMO in Fig 5.6. Analogous to Fig 5.6 we therefore identify this MO as the top of the "valence states". One full circle in Figure 5.7 indicates an extra "conduction electron". If this is compared to Fig 5.6, it can be seen that the LUMO, identified as the bottom of the "conduction states", is now occupied by the excess "conduction electron". In both cases this MO is of mixed tin-hydrogen origin.

![Diagram](image)

Figure 5.7 Generalised gradient corrected MO diagram around the HOMO-LUMO gap of [Sn\(_2\)O\(_{10}\)H\(_{10}\)]\(^{3-}\) molecular cluster of relaxed geometry. The molecular orbital with two full circles is the highest fully occupied orbital, the molecular orbital with one full circle is the singly occupied orbital.
5.3.2 Ru-modified clusters

(110) SnO₂ hydroxylated surface was modeled by the two clusters [Sn₂O₁₀H₁₀]²⁻ or [Sn₁₀O₄₀H₃₄]⁶⁻ of increasing size. The 2-fold Ru coordination site was modeled as bridging the two oxygens of the former terminal hydroxyl groups with one Ru atom for [Sn₂O₁₀H₁₀]²⁻ cluster and two Ru atoms for [Sn₁₀O₄₀H₃₄]⁶⁻. Hydrogen atoms were removed from terminal hydroxyl groups and a Ru atom was attached to those oxygen atoms, employing the Ru-O distance of 2.047Å found by EXAFS (see chapter 4).

(i) LDA calculations on unreconstructed Ru modified clusters of increasing size.

In the following calculations on the two clusters of increasing size only the positions of the Ru atoms and the surface oxygen atoms to which they were bound were relaxed. All other heavy atoms were fixed. Positions of all hydrogen atoms were optimized in every set of calculations. The double-zeta basis sets were used for all atoms, with the LDA approach to the exchange-correlation density functional.

MO energy levels for the two Ru modified clusters of increasing size are given in Fig 5.8. Filled circles indicate the highest occupied level. The “band gap” is set between the top of occupied “valence states” (HOMO) and the bottom of “conduction states”. Analogous to the unmodified case, the “conduction states” are identified as mixed tin-hydrogen derived orbitals. The appearance of a number of unoccupied gap orbitals below the “conduction” orbitals can be noted in each case, which are evidently induced due to Ru-O interaction. Note that the LUMO is now within the “band gap”, about 0.25-0.35eV above the top of the valence states.

Table 5.3 summarizes the compositions of the low lying unoccupied gap orbitals for each model. The surface oxygen atoms bound to Ru are marked in bold for convenience.
Table 5.3 LDA eigenvalues and atomic compositions for the low lying unoccupied gap orbitals for [Sn$_2$O$_{10}$H$_3$Ru]$^2^-$ and [Sn$_{10}$O$_{40}$H$_{30}$Ru$_2$]$^{6^+}$ clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>orbital</th>
<th>Energy/eV</th>
<th>Composition/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Sn$<em>2$O$</em>{10}$H$_3$Ru]$^2^-$</td>
<td>10a$_2$</td>
<td>3.786</td>
<td>61Ru$<em>{4d}$, 35O$</em>{2p}$</td>
</tr>
<tr>
<td>[Sn$<em>{10}$O$</em>{40}$H$_{30}$Ru$_2$]$^{6^+}$</td>
<td>53b$_1$</td>
<td>10.213</td>
<td>59Ru$<em>{4d}^{81}$, 22O$</em>{2p}^{49}$, 13O$_{2p}^{47}$</td>
</tr>
<tr>
<td></td>
<td>48a$_2$</td>
<td>10.283</td>
<td>60Ru$<em>{4d}^{81}$, 20O$</em>{2p}^{49}$, 16O$_{2p}^{47}$</td>
</tr>
</tbody>
</table>

$C_{2v}$ symmetry notation is used to label the orbitals. The number superscripts at the atomic symbols correspond to their location in the cluster from Fig 5.4. Each superscript implies all atomic species connected by $C_{2v}$ symmetry. The oxygen atoms bound to Ru are in bold.

Figure 5.8 LDA MO diagrams around the “band gap” of (a) [Sn$_2$O$_{10}$H$_3$Ru]$^2^-$, and (b) [Sn$_{10}$O$_{40}$H$_{30}$Ru$_2$]$^{6^+}$ molecular clusters. The HOMO is indicated by two full circles and the “band gap” is set between the HOMO and the lowest unoccupied MO of tin-hydrogen character.
Note that in each case independent of the cluster size the lowest unoccupied gap orbitals arise due to mixing of Ru 4d and surface oxygen 2p orbitals and are largely localized on the surface Ru atoms. Qualitatively speaking, increasing in the cluster size does not alter the modifications in electronic structure caused by the attached Ru.

(ii) Gradient corrected calculations on fully relaxed \([Sn_2O_{10}HgRu]^\pm\) cluster.

In the next series of calculations we include GGC for exchange and correlation energy and use extended triple-zeta basis sets for all atoms, we also consider the full surface relaxation, where the positions of all heavy atoms were relaxed to equilibrium within the constraints of \(C_2v\) symmetry. Qualitative features of electronic structure modifications caused by the attached Ru were examined and compared to those obtained with LDA. The calculations were done on the smallest cluster \([Sn_2O_{10}HgRu]^\pm\).

The calculated electronic structure for the fully relaxed Ru modified \([Sn_2O_{10}HgRu]^\pm\) cluster is depicted in Fig 5.9. The “band gap” is set between the HOMO and the LUMO of mixed tin-hydrogen character. The GGC calculations yield a number of unoccupied gap orbitals induced by Ru-O interaction and the LUMO is now within the band gap 0.25eV above the top of the “valence” orbitals. Table 5.4 summarizes the composition of the unoccupied gap orbitals lying in the bottom half of the “band gap” (above the HOMO). The surface oxygen atoms are marked in bold for convenience.

Table 5.4 GGC eigenvalues and atomic compositions for the lowest unoccupied energy levels for \([Sn_2O_{10}HgRu]^\pm\) cluster.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>orbital</th>
<th>Energy /eV</th>
<th>Composition /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>([Sn_2O_{10}HgRu]^\pm)</td>
<td>10(a_2)</td>
<td>2.679</td>
<td>63Ru(4d), 34O(2p)^9</td>
</tr>
<tr>
<td></td>
<td>15(b_1)</td>
<td>3.595</td>
<td>60Ru(4d), 33O(2p)^9</td>
</tr>
</tbody>
</table>

\(C_2v\) symmetry notation is used to label the orbitals. The number superscripts at the atomic symbols correspond to their location in the cluster from Fig 5.4. Each superscript implies all atomic species connected by \(C_2v\) symmetry. The oxygen atoms bound to Ru are in bold.
Figure 5.9 Generalised gradient corrected MO diagram around the “band gap” of $[\text{Sn}_2\text{O}_{10}\text{H}_{10}\text{Ru}]^{2-}$ molecular cluster of relaxed geometry. The HOMO is indicated by two full circles and the “band gap” is set between the HOMO and the lowest unoccupied MO of tin-hydrogen character.

The low lying molecular orbitals in the gap can be seen to be induced by Ru-O(surface) interaction and are largely localized on the surface Ru atom. The results of gradient corrected calculations are qualitatively similar to electronic structure modifications obtained with LDA for the Ru modified cluster.

In the final calculations in this section we introduce an extra charge into the Ru modified $[\text{Sn}_2\text{O}_{10}\text{H}_{10}]^{2-}$ system to imitate an extrinsic “conduction electron”. The calculations were performed using extended triple-zeta basis sets for all atoms and GGC for exchange and correlation energy, and allowing full cluster relaxation within the constraints of $C_{2v}$ symmetry. A series of calculations was performed, where the excess charge first was considered to occupy the Ru-O gap orbitals (fig 5.9), and then the lowest unoccupied tin-hydrogen orbital, as would be the case in the absence of Ru. The bonding energies (BE) computed in each case, with respect to the constituent fragments, are given in Table 5.5.
Table 5.5 Bonding energies (BE) for \([\text{Sn}_2\text{O}_{10}\text{H}_4\text{Ru}]^{3-}\) and varying orbitals occupancy. Orbital notation corresponds to Figure 5.9.

<table>
<thead>
<tr>
<th>Singly occupied MO</th>
<th>Composition /%</th>
<th>BE/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>10(a_2)</td>
<td>70Ru(4d;) 28O(2p^9)</td>
<td>-117.04</td>
</tr>
<tr>
<td>15(b_1)</td>
<td>68Ru(4d;) 25O(2p^9)</td>
<td>-116.59</td>
</tr>
<tr>
<td>16(b_1)</td>
<td>11Sn(3p;) 42Sn(3p;) 36H(1^{13};) 14H(1^{19})</td>
<td>-113.72</td>
</tr>
</tbody>
</table>

C\(v\) symmetry notation is used to label the orbitals. The number superscripts at the atomic symbols correspond to their location in the cluster from Fig 5.4. Each superscript implies all atomic species connected by C\(v\) symmetry. The oxygen atoms bound to Ru are in bold.

![Figure 5.10 Generalised gradient corrected MO diagram around the "band gap" of \([\text{Sn}_2\text{O}_{10}\text{H}_4\text{Ru}]^{3-}\) molecular cluster of relaxed geometry. The molecular orbital with two full circles is the highest fully occupied orbital, the molecular orbital with one full circle is the singly occupied orbital. The "band gap" is set between the HOMO and the lowest unoccupied MO of tin-hydrogen character. Binding energy, referenced to the free atoms, is also given.](image-url)

The minimum energy configuration was found with the excess electron occupying the LUMO Ru-O orbital in the gap. Fig 5.10 shows the calculated orbital diagram where two full circles indicate the highest fully occupied level or, analogous to Fig 5.9, the top of the valence states and one full circle indicate an extra "conduction electron". The "band gap" is also shown. The excess "conduction electron" can be seen to occupy the LUMO in the gap above the top of the valence states, which is largely localized on the attached Ru atom.
5.3.3. Interaction of gaseous molecules with surface attached Ru centre.

The results reported so far demonstrate that both LDA calculations and more sophisticated gradient corrected calculations yield qualitatively similar information on electronic structure modifications induced by the attached Ru. Chemical interaction of an adsorbate molecules with surface Ru is a local interaction, involving largely the Ru-gas molecule pairs, therefore LDA calculations involving the Ru modified \([\text{Sn}_2\text{O}_{10}\text{H}_{10}]^{2-}\) cluster are believed to be sufficient to qualitatively describe the trends in charge redistribution over the localized Ru-O molecular orbitals positioned in the “band gap”. The calculations were performed with double-zeta basis sets for all atoms, and the positions of the surface oxygen atoms bound to the Ru as well as the positions of the Ru atom itself and adsorbent species were reoptimized in each case. The structure of attached Ru centre and the species adsorbed onto Ru is referred to as the “surface fragment” and the surface oxygens bound to Ru are considered separately.

First an \(\text{O}_2\) molecule with O-O bond distance of 1.2 Å [184] was attached over the Ru atom with the O-O axis oriented along the x direction (Fig 5.11) and the positions of all atoms of the surface fragment and the surface oxygens were optimized by energy minimization. The oxygen molecule was then forced to dissociate (O-O distance was set to 3.2) and the minimum energy geometry was computed again, relaxing the positions of all atoms in the surface fragment and surface oxygens.

![Figure 5.11 Schematic diagram drawn as to emphasize the tetrahedral arrangement of (a) molecular oxygen, and (b) atomic oxygen; over the attached Ru.](image-url)
Table 5.6 summarizes the LDA bond distances obtained in the two cases. The bonding energies (BE) with respect to the constituent fragments are also given.

<table>
<thead>
<tr>
<th>Oxygen arrangement</th>
<th>Ru-O (O₂)/Å</th>
<th>O-O (O₂)/Å</th>
<th>BE/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-dissociative</td>
<td>1.944</td>
<td>1.564</td>
<td>109.77</td>
</tr>
<tr>
<td>Dissociative</td>
<td>1.781</td>
<td>3.294</td>
<td>112.79</td>
</tr>
</tbody>
</table>

Interaction of a O₂ molecule with the attached Ru centre gave a local energy minimum with non-dissociated geometry. The O-O distance increased to 1.564Å, compared to 1.2Å in a free molecule. However, even lower bonding energy was found when a fully dissociated arrangement of oxygens over Ru centre was enforced.

The full reaction path was then computed by gradually increasing the O-O bond distance and reoptimizing the geometry at each step. The energy profile for the reaction of O₂ dissociation over the surface Ru atom is given in Fig 5.12. Note that an energy barrier of at least 1.4 eV corresponding to the O-O distance of 1.66Å, indicates that O₂ dissociation is an activated process. For room temperature interaction (as in this work) we feel it is sensible to adopt non-dissociated adsorption.

![Figure 5.12 LDA energy profile for the reaction of O₂ dissociation over the attached Ru atom. Bond energy, referenced to the free atoms, is plotted against O-O distance. A region between the points 1 and 2 was not attempted and is represented by a dotted line.](image-url)
Finally interactions of CO and OH groups with the Ru centre were studied. Two arrangements were considered in the case of CO (Fig 5.13). First a single CO molecule was fixed over a Ru atom “atop” with C end down and secondly two CO molecules were arranged over the surface Ru in the XZ plane. Finally two OH groups were fixed over the Ru centre in the XZ plane (Fig 5.13). Electronic structures were computed for the optimized geometry in each case where the positions of all atoms of the surface fragment and surface oxygens were relaxed.

![Diagram](image)

Figure 5.13 Schematic diagram drawn as to emphasize the arrangement of (a) CO adsorbent molecules, and (b) hydroxyl groups over the attached Ru.

The LDA Ru-O bond distances, obtained for the cluster with the attached Ru(OH)$_2$ surface fragment, are compared in Table 5.7 to those measured by EXAFS for the hydroxylated Ru modified reduced sample (Chapter 4).

Table 5.7 Ru-O bond distances obtained by LDA calculations on the {[Sn$_2$O$_{10}$H$_8$]Ru-(OH)$_2$}$_2^-$ cluster and measured by EXAFS for the hydroxylated Ru modified reduced sample.

<table>
<thead>
<tr>
<th>Probe</th>
<th>LDA Ru-O(surface)</th>
<th>LDA Ru-O (OH)</th>
<th>EXAFS Ru-O (Average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru - O/Å</td>
<td>1.846</td>
<td>1.961</td>
<td>2.047± 0.008</td>
</tr>
</tbody>
</table>
The LDA Ru-O bond distances are lower than the EXAFS experimental value. A typical feature of LDA is to overbind [181] - i.e., produce bond lengths which are often short compared to experimental values.

Calculations on the Ru modified cluster with either CO, OH or O\textsubscript{2} species adsorbed onto the Ru centre yielded in each case an electronic structure characterized by a "band gap" (between the highest occupied energy level and the first unoccupied energy level of mixed tin-hydrogen character) of about 1.5-2eV and a number of molecular orbitals lying in the gap. Table 5.8 summarizes the atomic compositions of the lowest unoccupied orbitals, positioned in the gap, \Delta eV above the HOMO, for each considered structure of the surface fragment. The surface oxygen atom is marked in bold for convenience.

<table>
<thead>
<tr>
<th>Adsorbent Species</th>
<th>LU orbital</th>
<th>( \Delta ) /eV</th>
<th>Composition /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>10a\textsubscript{2}</td>
<td>0.37</td>
<td>35O\textsubscript{2p}\textsuperscript{9}, 61Ru\textsubscript{4d}</td>
</tr>
<tr>
<td>CO</td>
<td>10a\textsubscript{2}</td>
<td>0.54</td>
<td>42O\textsubscript{2p}\textsuperscript{9}, 50Ru\textsubscript{4d}</td>
</tr>
<tr>
<td>CO+CO</td>
<td>17b\textsubscript{1}</td>
<td>0.29</td>
<td>26O\textsubscript{2p}\textsuperscript{9}, 29Ru\textsubscript{4d}, 7Ru\textsubscript{5p}, 7O\textsubscript{2p}\textsuperscript{13}, 18C\textsubscript{1s}, 9C\textsubscript{2p}</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>23a\textsubscript{1}</td>
<td>0.04</td>
<td>21O\textsubscript{2p}\textsuperscript{9}, 52Ru\textsubscript{4d}, 7Ru\textsubscript{5p}, 4Ru\textsubscript{5p}, 9O\textsubscript{2p}\textsuperscript{13}</td>
</tr>
<tr>
<td>OH+OH</td>
<td>23a\textsubscript{1}</td>
<td>0.27</td>
<td>14O\textsubscript{2p}\textsuperscript{9}, 40Ru\textsubscript{4d}, 10Ru\textsubscript{5s}, 17H\textsubscript{1s}\textsuperscript{23}, 7O\textsubscript{2p}\textsuperscript{13}</td>
</tr>
</tbody>
</table>

\( \text{C}_{2\text{v}} \) symmetry notation is used to label the orbitals. The number superscripts at the atomic symbols correspond to their location in the cluster from Fig 5.4. Each superscript implies all atomic species connected by \( \text{C}_{2\text{v}} \) symmetry. The oxygen atoms bound to Ru are in bold.

Note that as a result of adsorption of a single CO molecule onto clean Ru sites the weight of the lowest unoccupied MO positioned in the "band gap" on the surface oxygen atoms increased, compared to the "clean" Ru case. Adsorption of molecular oxygen onto the clean Ru site, on the other hand, resulted in further localization of the Ru-O LUMO on the surface fragment.
Table 5.9 summarizes the bonding energies for the interaction of the surface Ru with each adsorbent species. As the bonding energies are the total binding energies with reference to those of constituent fragments, the BE for the free adsorbent molecules were also computed and are given in Table 5.9.

Table 5.9 Total bond energies for \([\text{Sn}_2\text{O}_{10}\text{H}_8\text{Ru}]^2\) cluster following adsorption of various species onto Ru. The bond energies for free adsorbent molecules are also given.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>BE/eV</th>
<th>Free species</th>
<th>BE/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Sn}<em>2\text{O}</em>{10}\text{H}_8\text{Ru}]^-)</td>
<td>-106.16</td>
<td>O₂</td>
<td>-8.59</td>
</tr>
<tr>
<td>([\text{Sn}<em>2\text{O}</em>{10}\text{H}_8\text{Ru}]\text{Ru-O}_2)^2⁻</td>
<td>-118.12</td>
<td>CO</td>
<td>-13.96</td>
</tr>
<tr>
<td>([\text{Sn}<em>2\text{O}</em>{10}\text{H}_8\text{Ru}]\text{Ru-CO})^2⁻</td>
<td>-122.17</td>
<td>OH</td>
<td>-7.20</td>
</tr>
<tr>
<td>([\text{Sn}<em>2\text{O}</em>{10}\text{H}_8\text{Ru}]\text{Ru-(CO)}_2)^2⁻</td>
<td>-139.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Sn}<em>2\text{O}</em>{10}\text{H}_8\text{Ru}]\text{Ru-(OH)}_2)^2⁻</td>
<td>-128.19</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From the above table it follows that one CO should not substitute for an adsorbed O₂ molecule:

\[
\{[\text{Sn}_2\text{O}_{10}\text{H}_8\text{Ru}]\text{O}_2\}^2^- + \text{CO} \quad \leftrightarrow \quad \{[\text{Sn}_2\text{O}_{10}\text{H}_8\text{Ru}]\text{Ru-CO}\}^2^- + \text{O}_2
\]

\[
\text{BE} = -132.08\text{eV} \quad \text{BE} = -130.76\text{eV}
\]

However an adsorbed O₂ molecule might be substituted by two CO species:

\[
\{[\text{Sn}_2\text{O}_{10}\text{H}_8\text{Ru}]\text{O}_2\}^2^- + 2\text{CO} \quad \rightarrow \quad \{[\text{Sn}_2\text{O}_{10}\text{H}_8\text{Ru}]\text{Ru-(CO)}_2\}^2^- + \text{O}_2
\]

\[
\text{BE} = -146.04\text{eV} \quad \text{BE} = -147.61\text{eV}
\]

Referring back to Table 5.8 it appears that the surface oxygen atoms’ contribution to the lowest unoccupied eigenstate slightly increases on substitution of O₂ with two CO.
The two OH groups adsorbed onto the Ru centre, however, would not be displaced, as the arrangement appears to be energetically favored with respect to O$_2$ and CO species.

\[
\begin{align*}
\{[\text{Sn}_{2}\text{O}_{10}\text{H}_8]\text{Ru}-(\text{OH})_2\}^2+\text{O}_2 & \leftrightarrow \{[\text{Sn}_{2}\text{O}_{10}\text{H}_8]\text{Ru}-\text{O}_2\}^2+2\text{OH} \\
& \text{BE} = -136.78\text{eV} \quad \text{BE} = -135.52
\end{align*}
\]

\[
\begin{align*}
\{[\text{Sn}_{2}\text{O}_{10}\text{H}_8]\text{Ru}-(\text{OH})_2\}^2+2\text{CO} & \leftrightarrow \{[\text{Sn}_{2}\text{O}_{10}\text{H}_8]\text{Ru}-(\text{CO})_2\}^2+2\text{OH} \\
& \text{BE} = -156.11\text{eV} \quad \text{BE} = -153.42\text{eV}
\end{align*}
\]

Referring again to table 5.8, note that in the case of the two OH species bound to the surface Ru centre, the maximum degree of localization of the lowest unoccupied gap state on the surface fragment is obtained.
5.4 Discussion.

We should point out again that our molecular cluster calculations are only intended to probe the general qualitative trends in electronic structure modifications caused by Ru grafting and subsequent gas chemisorption onto supported Ru, with the aim of shedding light on the experimentally observed room temperature gas sensitive electrical behaviour from surface grafting of the Ru onto SnO$_2$-0.2\%Sb. In particular we did not attempt to calculate an actual electronic structure of hydroxylated SnO$_2$-0.2\%Sb surface, or reproduce any quantitative results obtained experimentally.

The initial calculations on the Ru free molecular clusters, chosen to model the hydroxylated SnO$_2$(110)surface, were carried out to identify the common features of the unmodified electronic structure so that the effect of attached Ru could be isolated. It appeared that in both LDA and GGC calculations and independently of the cluster size, the electronic structure of an unmodified cluster displayed occupied “valence” orbitals built from oxygen 2p atomic orbitals, separated by a HOMO-LUMO energy gap of over 1.5eV from unoccupied “conduction” orbitals of mixed hydrogen-tin character.

Our representation of the electronic structure of hydroxylated SnO$_2$(110) surface is quite simplistic and reflects limitations of the cluster size and chosen embedding, but in qualitative terms it is clearly adequate to describe the absence of the electrical conductivity at moderate temperatures, due to the high excitation energy required to promote the charge carriers from the “valence” orbitals into the “conduction” orbitals across a substantial energy gap.

The general features of electronic structure, characteristic for the unmodified case, were retained on Ru grafting. Similarly to the unmodified case, both GGA and LDA calculations on the Ru modified clusters, independently of the size of the basis set or the cluster size, yield an energy gap of over 1.5eV between occupied “valence” orbitals and unoccupied “conduction” orbitals. However, all calculations also gave extra unoccupied molecular orbitals positioned in the gap, which appear to be a result of hybridization of components of Ru 4d orbitals with surface O 2p levels.
The variation in the position of the Ru-O trap molecular orbitals within the energy gap is of less concern. The significant points are that all calculations give qualitatively similar structures within the “band” gap and the origin of the gap orbitals, placing the LUMO Ru-O state low in the bottom half of the “band” gap. We concentrated on the effect of such electronic structure modification induced by Ru-O(–Sn) interaction on the supposed electrical conductivity of the chosen cluster models.

The lowest unoccupied molecular orbitals, positioned in the bottom half of the “band” gap above the HOMO are largely of Ru d character, and it can be said that electrons occupying these orbitals are mainly localized on the attached Ru. We have demonstrated, by introducing an extra charge, that the excess electron from the “conduction” tin-hydrogen derived orbital (as in the Ru free case) now occupies the previously LUMO orbital, positioned within the energy gap, and is therefore trapped on the Ru atom. The depletion of the “conduction” orbitals of the charge carriers is expected to result in lower electrical conductivity of the model system.

The electronic interaction between the attached Ru and the molecular cluster, chosen to model SnO₂ support, occurs through surface oxygen atoms due to a direct Ru-O(–Sn) chemical bonding. It should be noted that although the Ru-O LUMO, positioned in the gap, is largely localized on the attached Ru atom it also has partial surface oxygen character, and consequently some of the character of the supporting oxide. Changes in the electrical conductivity of the material could be then predicted by examining the extent of localization of the Ru-O trap orbitals on the attached Ru. If the weight of the Ru-O LUMO on the surface oxygen atoms increases, the degree of localization of the excess charge, trapped into this orbital, on the grafted Ru would decrease. As a result, charge redistribution over the Ru-O orbital with partial charge donation from the attached Ru to the surface oxygen atoms would be expected. The described charge donation would be felt by the surface Sn cations bound to those surface oxygens, and is expected to be reflected in an electrical conductivity increase.
LDA calculations on the Ru modified cluster showed that gas chemisorption onto Ru centres induced variations in the composition of the Ru-O trap orbital positioned in the gap, implying charge redistribution. Thus a conductivity increase is expected on adsorption of a single CO molecule onto the clean Ru centre, as the degree of localization of the excess charge on the surface Ru decreases. This is in agreement with our experimental results, where the resistance response to CO was recorded in oxygen free conditions.

Dissociation of molecular oxygen over the supported Ru was found to be an activated process with an activation energy over 1.5eV. It is believed therefore that at ambient temperatures oxygen adsorbs non-dissociatively onto surface Ru centres. This is in agreement with our XPS results, discussed in Chapter 4, where only slight partial oxidation was recorded on exposure of the supported Ru samples to oxygen in dry air. Our calculations also yield further Ru-O trap orbital localization on the surface fragment on molecular oxygen chemisorption, which would be expected to cause a conductivity decrease. Experimentally we have indeed observed an electrical resistance increase for the Ru modified material in dry air.

From thermodynamic considerations it appears that an O$_2$ molecule adsorbed onto the supported Ru would be replaced by two, not one, CO molecules. As a result of such substitution the weight of the lowest unoccupied Ru-O trap orbital within the energy gap on the surface oxygen atoms was shown to increase slightly. An excess charge trapped onto the state would therefore be a little less localized on the surface fragment, resulting in a small conductivity increase.

The resistance response to CO in the presence of oxygen in the dry air, measured experimentally, was actually quite small, compared to that in oxygen free conditions. Weakening of the resistance response to CO in the presence of oxygen, where Ru adsorption sites are precovered with chemisorbed molecular oxygen, would also be expected from steric considerations. Substitution of the adsorbed O$_2$ with two CO species would most probably proceed in two stages. In the first instance a single CO would be expected to adsorb onto a vacant Ru coordination site. This should cause some bending of Ru-O$_2$ bond due to repulsion of adsorbate species and also weakening of Ru-O$_2$ interaction.
The second CO could then substitute for $O_2$. The process would evidently require substantial activation in the first instance and is expected to be rather slow.

As a result of interaction of OH groups with the attached Ru the Ru-O LUMO became strongly localized on the surface fragment. An even greater decrease in the electrical conductivity would therefore be expected, compared to that caused by adsorbed molecular oxygen. Our calculations yield that the adsorption of OH groups onto supported Ru was energetically favoured over molecular oxygen and CO. The adsorbed OH groups therefore inhibit subsequent chemisorption of either $O_2$ or CO. Experimentally we have shown that exposure to moisture of the Ru modified material resulted in an irreversible resistance increase and the loss of CO resistance response.

Thermodynamically the hydroxylated surface fragment was found to be the most stable arrangement. This arrangement corresponds to a Ru coordination number of 4, with oxidation state of the supported Ru being +4. This is in agreement with our XPS and EXAFS findings (Chapter 4), where a coordination number of 4.3 was reported and the supported Ru was found in the +4 oxidation state, following contact with moisture in air.
Chapter 6.

Preliminary Results on Further Surface Modification

6.1 Objectives

In the final part of this work we set about to test the generality of the effect of modified gas sensing behaviour in semiconducting oxides induced by surface modification.

6.2 Experimental

6.2.1 Preparation

Preparation of SnO$_2$-0.2%Sb was described in Chapter 2.

BaSn$_{0.97}$Sb$_{0.03}$O$_3$ and BaFeO$_{3-x}$ studied here were prepared by a conventional ceramic route. The correct stoichiometric amounts of appropriate oxides/carbonates: Fe$_2$O$_3$ (Fluka, >99% pure), Sb$_2$O$_3$ (Aldrich, 99.995% pure), SnO$_2$ (Aldrich, 99.995% pure) and BaCO$_3$ (Fluka, >99% pure) were mixed in a ball mill with acetone and ceramic beads for 24 hours. The mixtures were then evaporated and fired at 1200°C for 12 hours in air.

Pure TiO$_2$ is an insulator at room temperature and therefore Nb(V) doping was used to increase electrical conductivity of titania. TiO$_2$-10at%Nb was prepared by hydrolysis of stoichiometric solution of Titanium Isopropoxide (Aldrich, 99.9999%pure) and Niobium Ethoxide (Aldrich, 99.995% pure) in methanol, for which water was slowly added under vigorous stirring conditions. The white precipitate which was formed was separated on centrifuge, washed and dried at 120°C overnight, followed by calcination in air at 600°C for 12 hours.
Pt surface decoration

The resultant compounds of BaSn_{0.97}Sb_{0.03}, BaFeO_{3-x} and TiO_{2-10at %}Nb were loaded with Pt to produce 10% formal monolayer (ML) Pt coverage, using wetness impregnation as described in Chapter 3. The appropriate mass % of Pt (Fig. 3.1) was taken each time to form the required formal monolayer coverage.

Ti surface grafting

Ti precursor solution

The route was through the preparation of a reactive organometallic Ti complex, which would react readily with surface functional OH groups and from which the remaining ligands could subsequently be removed by calcination.

\[(\eta_5-C_5H_5)_2TiCl_2\] (Aldrich) was mixed with AgBF_{4} (1:1) and 10cm³ of anhydrous acetone for one hour at room temperature under argon. The solution was filtered through celite four times to remove the precipitate of AgCl. The red solution of what is believed to be \[\left[(\eta_5-C_5H_5)_2TiCl(acetone)\right]^+ BF_4^-\] was used in further preparations.

Support pretreatment

The SnO_{2-0.2%}Sb and TiO_{2-10%}Nb supports were pretreated following the procedure, described in Chapter 4.

200mg of powdered pretreated SnO_{2-0.2at%}Sb or TiO_{2-10%}Nb were mixed into 10ml of the Ti precursor solution without exposure to ambient air and stirred over night at room temperature. Unreacted solution in each case was removed carefully by repeatedly subjecting the mixtures to centrifugal force, removing the solution and adding acetone. The final mixtures were filtered and the supported samples were pelletized under a pressure of 1000kg into 13mm diameter disks 1-2mm thick and studied.
6.2.2 Supported materials pretreatment.

*Platinized samples*

Pelletized samples were calcined in dry air at 340°C for 1 hour to decompose the Pt salt and cooled down to room temperature in dry air. As we have demonstrated earlier (Ch3), such decomposition conditions resulted in maximum CO sensitivity at room temperature.

*Ti surface-modified samples*

Following Maschmeyer *et al* [119] supported Ti samples were heated up to 400°C in pure N₂, the gas was then changed to O₂ and the powders were calcined in dry oxygen at 500°C for 1 hour to remove the cyclopentadienyl ligand and cooled down in dry oxygen to room temperature.

6.2.3 Materials Characterization.

(i) **Gas sensitivity measurements.**
Electrical resistance response to carbon monoxide at room temperature was investigated in dry and moist air. Prior to gas sensitivity measurements samples were pretreated *in situ*, as described above.

(ii) **X-ray powder diffractometry.**
X-ray powder diffractometry was performed on Siemens D50000 in transmission mode with incident beam monochromator and Cu-Kα radiation. Samples of BaSn₀.₉₇Sb₀.₀₃O₃ , BaFeO₃₋ₓ and TiO₂₋₁₀%Nb were examined and the XRD spectra are given in Fig 6.1. In the case of BaSn₀.₉₇Sb₀.₀₃O₃ powder diffractometry showed the presence of a single well crystallized perovskite phase. BaFeO₃₋ₓ was characterized by a single phase structure of barium iron oxide. The crystal structure of TiO₂₋₁₀%Nb was identified as anatase. Broad diffraction peak signifies a very fine crystallite size.
Figure 6.1 Powder diffraction patterns for (a) BaSn_{0.97}Sb_{0.03}O_{3+}, (b) BaFeO_{3+}, and (c) TiO_{2-10\%}Nb.
(iii) X-ray photo electron spectroscopy

Platinized samples

Al Kα excited photoemission spectra were taken on the stannate and ferrate based samples, following their decomposition and exposure to room ambient. The object of the studies was to establish the surface composition of the sensors, to evaluate the level of the surface Pt loading and to determine the variations in the valence band structure induced by Pt. The binding energies were referenced to the hydrocarbon C 1s peak at 284.80 eV [139] and the sample charging was controlled with a 4eV flood gun. Spectrum quantification was performed following the route described in Chapter 3.

Ti supported samples

Al Kα excited photoemission spectra were taken on the SnO₂-0.2%Sb^Ti sample, following its decomposition and exposure to the room ambient. The object of the studies was to establish the surface composition of the sensor and in particular to verify the Ti surface loading. The binding energies were referenced to the hydrocarbon C 1s peak at 284.80 eV [139]. Spectrum quantification was performed following the route described in Chapter 3.

Ti surface loading in SnO₂-0.2%Sb^Ti was found to be about 4 at%Ti. The Ti surface species are believed to be characterized by a single oxidation state. The photoemission spectrum in the Ti2p region is given in Fig 6.2 and it can be seen that a single peak is required to fit the region, with Ti₁/₂:Ti₃/₂ set to 1:2 and (T₁/₂ :Ti₃/₂) binding energy separation set to 6.1eV [139]. A binding energy of 457.6eV can be assigned to Ti⁺⁺ species [187]. However, since only a preliminary examination was performed, identification of the correct chemical state and structure of the Ti surface species was not attempted.
Figure 6.2 XP spectra of the Ti 2p region for Ti modified SnO$_2$-0.2\%Sb porous pellet, following calcination.
6.3 Results

6.3.1 Platinized samples.

(i) Gas sensitivity.

Plot of the resistance variation with CO concentration and relative humidity in air vs time for the pure TiO$_2$-10%Nb sample is given in Fig 6.3, and for the platinized TiO$_2$-10%Nb is given in Fig 6.4. The measurements were performed at room temperature. The behaviour of the platinized sample was very similar to that of the pure TiO$_2$-10%Nb sample in response to relative humidity in air. A large resistance decrease was recorded on exposure of both samples to 50% relative humidity in air, with full recovery once dry air was reapplied. The unmodified sample, however, showed no resistance change in response to CO in air at room temperature. In the case of the platinized sample a modest resistance decrease was registered in dry air in response to ppm concentrations of CO in air. The effect was lost in 50% relative humidity, but was recovered on the next cycle, when dry air was reapplied.

![Figure 6.3](image-url)  
Figure 6.3 Time profile of the room-temperature resistance of TiO$_2$-10%Nb pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.
Figure 6.4 Time profile of the room-temperature resistance of Pt decorated TiO$_2$-10\%Nb pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50\% relative humidity) air.

The results of similar measurements, performed for the platinized BaSn$_{0.97}$Sb$_{0.03}$O$_3$ at room temperature are given in Fig 6.5. Note that the stannate showed reduced sensitivity to moisture, compared to similarly treated platinized SnO$_2$-0.2\%Sb (Fig 3.7, c) or platinized TiO$_2$-10\%Nb, above. A resistance response to CO was recorded in both moist and dry air and there was no effect of moisture on the magnitude of the CO response. Metal free BaSn$_{0.97}$Sb$_{0.03}$O$_3$ showed no gas sensitive electrical conductivity at room temperature.
The comparison plot of resistance variation with CO concentration in dry air at room temperature vs time for the platinized samples of BaSn$_{0.97}$Sb$_{0.03}$O$_3$, BaFeO$_{3-x}$, and TiO$_2$-10%Nb is given in Fig. 6.6. The BaFeO$_3$ based sample showed no room temperature CO resistance response.

Figure 6.5 Time profile of the room-temperature resistance of Pt decorated BaSn$_{0.97}$Sb$_{0.03}$O$_3$ pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.

Figure 6.6 Time profile of the room-temperature resistance of Pt decorated (a) BaSn$_{0.97}$Sb$_{0.03}$O$_3$, (b) BaFeO$_{3-x}$, and (c) TiO$_2$-10%Nb pellets as a function of exposure to ppm concentrations of CO in dry
Table 6.1 summarizes the values of the resistance response, $S$, to 1000ppm CO for the above samples.

Table 6.1 Resistance response, $S$, to 1000ppm CO in dry air for platinized BaSn$_{0.97}$Sb$_{0.03}$O$_3$ and TiO$_2$-10%Nb.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{1000\text{ppm CO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSn$<em>{0.97}$Sb$</em>{0.03}$O$_3$</td>
<td>2.56</td>
</tr>
<tr>
<td>TiO$_2$-10%Nb</td>
<td>0.33</td>
</tr>
</tbody>
</table>

(ii) X-ray Photoelectron Spectroscopy

The surface composition of the metal free TiO$_2$-10%Nb sample was measured. Table 6.2 give the Nb surface content of the sample, compared to the bulk Nb content (taken as the amount of Nb added).

Table 6.2 Surface/bulk Nb content for TiO$_2$-10%Nb

<table>
<thead>
<tr>
<th>Probe</th>
<th>Nb at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk (added)</td>
<td>10</td>
</tr>
<tr>
<td>surface (XPS)</td>
<td>22</td>
</tr>
</tbody>
</table>

The sample surface was found to be Nb enriched.

The surface Pt loading for the BaSn$_{0.97}$Sb$_{0.03}$O$_3$ and FeSnO$_{3-x}$ samples, as found by XPS are summarized in Table 6.3.

Table 6.3 Surface Pt content (At%) for BaSn$_{0.97}$Sb$_{0.03}$O$_3$ and BaFeO$_{3-x}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt [at%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSn$<em>{0.97}$Sb$</em>{0.03}$O$_3$</td>
<td>1.09</td>
</tr>
<tr>
<td>BaFeO$_{3-x}$</td>
<td>1.44</td>
</tr>
</tbody>
</table>
In general the surface Pt loading was similar for the two samples, with perhaps a little higher value for BaFeO$_{3-x}$.

Al K$_\alpha$ excited photoemission spectra in the valence band region for the stannate and ferrate based platinized samples are given in Fig. 6.7. The spectrum for the Pt free stannate is also given. Pt electronic states were detected just above the valence band edge (at ca 2 eV lower binding energy) in the band gap of the Pt decorated stannate, along with the negative shift in the VB edge of about 0.3 eV. Note that in the spectrum of the ferrate Pt electronic states are overlapped by a very broad peak incorporating Fe 3d and 4s components, since the d- and s-bands of iron are located at binding energies of 0.7 and 3.0 eV respectively [188].

Figure 6.7 XP valence band spectra of (a) pure BaSn$_{0.97}$Sb$_{0.03}$O$_3$, (b) Pt decorated BaSn$_{0.97}$Sb$_{0.03}$O$_3$, and (c) Pt decorated BaFeO$_{3-x}$. 
The Al K$_\alpha$ excited photoemission spectrum of the valence band region for TiO$_2$-10\%Nb (Pt free) is given in Fig. 6.8. Although the platinized sample was not examined it can be seen that the valence band edge of the TiO$_2$-10\%Nb is at ca 3.5eV. No energy states were revealed in the band gap above the valence band edge, signifying that the near-Fermi level peak characteristic for Pt surface states would, if present, dominate the region.

![Figure 6.8 XP valence band spectrum of pure TiO$_2$-10\%Nb](image)

The photoelectron spectra of the Pt 4f region for the BaSno.97Sbo.03O$_3$ and BaFeO$_{3-x}$ samples are given in Fig 6.9 together with Pt 4f$_{7/2}$ binding energies for different Pt speciations [142,143]. In both cases the surface Pt can be characterized by mixture of Pt$^{4+}$, Pt$^{2+}$ and Pt$^0$.

![Figure 6.9 XP spectra of the Pt 4f region for the Pt decorated pellets of (a) BaSn$_{0.97}$Sb$_{0.03}$O$_3$, and (b) BaFeO$_{3-x}$](image)
6.3.2 Ti-modified samples

(i) Gas sensitivity.

Plot of the resistance variation with CO concentration and relative humidity in air vs time for the Ti$^\text{SnO}_2\cdot0.2\%\text{Sb}$ sample is given in Fig. 6.10. The measurements were performed at room temperature. On initial exposure of the dry sample to CO in dry air, following decomposition, no resistance response was recorded. On exposure to 50% relative humidity in air a large resistance decrease was observed; such behaviour is a well known characteristic of n-type tin dioxide [44], as was mentioned earlier (Fig. 4.8, Chapter 4). Similarly, as can be seen in Fig. 6.10, the resistance did not completely recover in dry air, following the exposure to moisture of the Ti$^\text{SnO}_2\cdot0.2\%\text{Sb}$ sample. Note, however, that following the exposure to moisture (where no CO resistance response was recorded) the sample showed a modest p-type resistance response to CO in dry air: on exposure of the “wet sample” to CO in dry air a resistance increase was recorded.

![Graph of resistance variation with CO concentration and relative humidity](image)

**Figure 6.10** Time profile of the room-temperature resistance of Ti modified SnO$_2$-0.2%Sb pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.
The effect, however, was lost again on subsequent exposure to 50% relative humidity in air. Fig 6.11 shows the continuation of the experiment for the subsequent dry air - moist air cycles. It can be seen that the p-type CO resistance response can be recovered every time in dry air, having been lost in moist air.

Figure 6.11 Time profile of the room-temperature resistance on the subsequent dry air-wet air cycles of the Ti modified SnO$_2$-0.2%Sb pellet (as per fig 6.10) as a function of exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.

The variation of the resistance with CO concentration and relative humidity at room temperature is shown in Fig 6.12 for the Ti modified TiO$_2$-10%Nb sample. Note the large resistance decrease in response to 50% relative humidity in air, which recovered when dry air was reapplied. Note also that for this system a CO resistance response could be registered in both dry and wet (50% relative humidity) air and it appears that the sensitivity to CO was not affected by the water vapor: a resistance decrease of the same order of magnitude in response to the presence of traces of CO was recorded. Table 6.4 summarizes the values for the resistance response, S, to 1000ppm CO in dry air at room temperature for Ti$^{+}$SnO$_2$-0.2%Sb and Ti$^{+}$TiO$_2$-10%Nb.
Table 6.4  Resistance response, S, to 1000ppm CO in air at room temperature for Ti^SnO2-0.2%Sb and Ti^TiO2-10%Nb.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{1000ppm CO}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti^SnO2-0.2%Sb</td>
<td>0.12</td>
</tr>
<tr>
<td>Ti^TiO2-10%Nb</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Figure 6.12  Time profile of the room-temperature resistance of a Ti modified TiO2-10%Nb pellet as a function of water vapor pressure and exposure to ppm concentrations of CO in dry and wet (50% relative humidity) air.
6.4 Discussion.

As was seen to be the case with platinized SnO$_2$-0.2\%Sb, decoration of the BaSn$_{0.97}$Sb$_{0.03}$O$_3$ surface with Pt resulted in a room temperature gas sensitive electrical conductivity. The effect was also observed for the 10\%Pt/TiO$_2$-10\%Nb, which is a non-tin containing oxide. In the case of 10\%Pt/BaSn$_{0.97}$Sb$_{0.03}$O$_3$ surface electronic states of Pt origin were identified in the band gap above the valence band edge, causing increase in the band bending of ca 0.3eV. It is believed that, similarly to platinized SnO$_2$-0.2\%Sb, the room temperature CO resistance response of the material is induced due to electronic interaction between the Pt additives and the oxide support.

Based on the Pt loading and the chemical state of the surface Pt, the electrical behaviour of the platinized BaFeO$_{3-x}$ could be expected to be similar to that of the other semiconducting oxides studied. However, it was demonstrated that this sample was not sensitive to CO at room temperature. The valence band spectrum of the ferrate was characterized by a broad peak at 5eV due to Fe 3d, which dominated the electronic structure of the material in the energy region typically characteristic for the Pt surface state energy. It is apparent that electronic effects due to charge transfer between the supported Pt and the oxide would be diminished in this case, resulting in the electrical conductivity being insensitive to interaction of gases with the supported Pt at room temperature.

We have demonstrated that the role of the Pt additives, finely dispersed over the semiconducting oxide surface, is to induce the room-temperature CO resistance response of the material. The effect, however, can only be observed in the case where the support response mechanism is dominated by electronic properties of the Pt, so that variations in the Pt chemical state modulates sensitively the semiconducting properties of the oxide.
Surface grafting of Ti onto SnO$_2$-0.2%Sb resulted in a modified gas sensing behaviour of the material. A p-type resistance response to CO was recorded at room temperature, which was only observed in dry air following exposure to moisture. A particularly interesting observation is the actual p-type response in the Ti modified SnO$_2$, since both materials are generally n-type semiconductors [33] and in an unmodified form show no gas sensitive electrical conductivity at room temperature.

The possible mechanism might be substitution of the adsorbed molecular water for CO at the Ti site. Since the effect is a resistance increase, it was dominated by a large resistance decrease in moist air - characteristic for SnO$_2$-0.2%Sb support - and no CO response could be observed in moist air. Maschmeyer et al [119] showed, that Ti$^{4+}$ centres, grafted onto mesoporous silica (MCM-41) were stable on exposure to ambient air. On contact with moisture, Ti$^{4+}$ centres were shown to coordinate the molecular water, but this did not effect the catalytic activity. The gas sensing behaviour of the Ti$^{4+}$SnO$_2$-0.2%Sb system is rather different from that observed for the Ru$^{4+}$SnO$_2$-0.2%Sb. Both systems, however, showed room temperature gas sensitive conductivity from surface grafting of the reactive centres onto oxide support.

We have also shown that the effect was not specific to SnO$_2$-0.2%Sb support, since surface grafting of Ti onto TiO$_2$-10%Nb also resulted in the room temperature gas sensitivity of the device. The interesting point here is that the surface-grafted Ti was evidently in a different chemical environment to the Ti of the oxide itself, at the surface. In this case, for the first time, the material was actually unaffected by the water vapor. The resistance response to CO was recorded in both moist and dry air. This system, so far, has proved to be particularly promising.
7. Summary and conclusion.

In this work we have sought to demonstrate the possibility of modulating the gas sensing characteristics of semiconducting oxides by functionalizing the surface with particular reactive centres which, being equivalent to surface electronic states positioned within the band gap, communicated electronically with the oxide so that variations in their chemical state due to gas chemisorption could be transduced into an electrical conductivity change at ambient temperature. Surface grafting techniques were used to provide reactive Ru and Ti surface centres connected electronically with the semiconducting oxide supports. Surface modification with Pt was performed by a simple wetness impregnation procedure. In general, surface engineering of SnO$_2$-0.2%Sb with Ru, Pt, Ti; of TiO$_2$-10%Nb with Pt, Ti; and of BaSn$_{0.97}$Sb$_{0.03}$O$_3$ with Pt in each case induced a room temperature gas sensitivity of the electrical conductivity with particular differences specific to each system. Grafting of Ti onto n-type SnO$_2$-0.2%Sb induced a p-type resistance response of the material to CO at room temperature. The Ti modified TiO$_2$-10%Nb showed room temperature gas response stable to variations in the water vapor pressure. The effect of the room temperature gas sensitive electrical conductivity from surface grafting of specific reactive centres onto oxide surface was demonstrated for the first time.

In particular Ru centres were anchored onto SnO$_2$-0.2%Sb surface via an interaction of organometallic Ru precursor with the surface functional groups on the tin dioxide support, followed by decomposition of the grafted complex to drive off the organic component. Decomposition in hydrogen produced reactive surface bound Ru centres in electronic contact with the tin dioxide support. Formation of surface bound Ru centres was confirmed by EXAFS and the electronic interaction was revealed by XPS, where Ru was shown to introduce states within the tin dioxide band gap lying 1.3eV above the valence band edge, and also by resistivity measurements, since the effect of SnO$_2$-0.2%Sb surface modification with Ru was to increase the room temperature resistivity of the material. The atmosphere induced variations in the electrical conductivity of the Ru modified SnO$_2$-0.2%Sb were correlated with variations in the chemical state of the attached Ru, caused by
gas chemisorption. TPD studies indicated gas interactions with the attached unsaturated Ru centres at room temperature: adsorption of CO, NO and oxygen was demonstrated.

Adsorption of CO and NO onto surface bound Ru centres resulted in a resistance decrease, whereas atmospheric oxygen interaction with the reactive Ru centres caused a positive baseline resistance drift induced by partial oxidation of the Ru. XPS studies revealed partial oxidation of the surface Ru on interaction with atmospheric oxygen. Exposure of the Ru modified sample to moisture in air resulted in a further resistance increase induced by further oxidation of the Ru. The effect of moisture on the electrical conductivity was shown to be irreversible. XPS analysis indicated formation of the hydroxylated Ru$^{4+}$ surface species and the EXAFS revealed the presence of four-coordinated Ru$^{4+}$ centres on the surface of the hydroxylated sample. Strongly bound OH groups inhibited subsequent gas interactions with the Ru surface centres and as a result the room temperature gas response was lost in ambient air. We have further demonstrated by EXAFS that decomposition in air of the grafted Ru organometallic complex resulted in the formation of the bulk RuO$_2$ particles on the SnO$_2$-0.2%Sb and in this case the gas sensitivity of the electrical conductivity was lost. We indicated that if the unsaturated reactive surface centres are destroyed by thermal oxidation, the electrical effects are also destroyed.

DFT molecular cluster calculations on Sn$_n$O$_m$H$_x$ clusters, chosen to model the Ru modified SnO$_2$ (110) surface, showed that electronic interaction between the attached Ru and the model cluster support occurred through surface oxygen atoms due to a direct Ru-O(-Sn) chemical bonding. Formation of Ru-O trap orbitals, positioned in the energy gap above the cluster HOMO were identified. These molecular orbitals were largely localized on the attached Ru atom with partial surface oxygen character. Interaction of gaseous molecules with the attached Ru resulted in variations in the Ru-O trap orbital composition. Changes in the degree of localization of the Ru-O orbital on the surface Ru atom were related to experimentally observed changes in electrical conductivity in response to gas adsorption onto grafted Ru centres.
For the Pt decorated SnO$_2$-0.2%Sb the electrical conductivity at room temperature was demonstrated to be controlled by the chemical state of the supported Pt. Exposure of the sample which exhibited only metallic Pt species to moisture in air caused partial oxidation of the surface Pt$^0$ to Pt$^{2+}$, which was detected by XPS. Partial oxidation of the supported Pt$^0$ on moisture exposure was reflected in the resistance increase of the material. The effect of the room temperature gas sensitivity of the electrical conductivity was demonstrated to be specific to the presence of Pt$^{2+}$ surface species. Supported metallic Pt was shown to be a good room temperature CO oxidation catalyst, but the material decorated with Pt$^0$ showed no CO resistance response. The effect of the room temperature CO response was assigned to specific CO chemisorption onto Pt$^{2+}$ sites, resulting in partial charge transfer and consequently reduction of the supported Pt, measured as a resistance decrease.

For the Pt decorated BaFeO$_{3-x}$ the conductance response mechanism was dominated by electronic properties of the support, rather than the surface Pt, as was indicated by XPS. In this case the gas sensitivity of the electrical conductivity at room temperature was lost.

In conclusion we have shown that surface tailoring of semiconducting oxides with organometallic precursors can be employed to achieve gas sensitivity of the electrical conductivity at room temperature. In this case the electrical conductivity can conceivably be used to monitor changes in the chemical state of the grafted centre caused by gas adsorption.
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