

Electron paramagnetic resonance characterization of ruthenium-dispersed tin oxide obtained by sol-gel and impregnation methods

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Ruthenium was dispersed in SnO₂ by cogelation of tin and ruthenium precursor compounds: tetra(*tert*-butoxy)-tin(IV), [Sn(OBu^t)₄], and tris(acetylacetonato)ruthenium(III) [Ru(acac)₃]. This resulted in samples with a controlled and reproducible metal/SnO₂ molar ratio (0.8). An electron paramagnetic resonance study on sample reactivity showed that: [Ru(acac)₃] was included in the SnO₂ gel without significant matrix-induced qualitative modifications of the coordination compound; thermal treatment of [Ru(acac)₃]-SnO₂ in air led to oxidation of most of the Ru³⁺ centres to diamagnetic Ru⁴⁺ centres; reduction with CO(0.5%)-argon at 773 K reformed all the original Ru³⁺ centres. In the CO-argon treated samples, the Ru³⁺ centres were in the field of oxide ligands; lower paramagnetic oxidation states, clustering effects and paramagnetic singly ionized oxygen vacancies (V_O⁺) were absent. It was concluded that a great many Ru⁴⁺ centres could substitute Sn⁴⁺ in samples prepared by cogelation, thus optimizing the intimacy of metal-semiconductor contact.

As an alternative to cogelation, ruthenium was more conventionally dispersed in SnO₂, impregnating the oxide with [Ru(acac)₃]. [Ru(acac)₃]-SnO₂-impregnated samples, thermally decomposed in air and reduced by CO(0.5%)-argon, gave fewer trivalent ruthenium centres and stable singly ionised oxygen vacancies, V_O⁺, were evident. This suggested that metal centre clustering took place and electron transfer from V_O⁺ to the metal was less efficient than in sol-gel prepared samples, due to the less intimate metal-semiconductor contact of the metal clusters.

Both types of ruthenium-dispersed tin oxide samples reacted with oxygen, the resultant amounts of Sn⁴⁺-O₂⁻ being much greater for the sol-gel prepared samples than for the impregnated analogues.

The sol-gel method of metal dispersion seemed much more efficient in preparing samples highly sensitive to both reducing and oxidising gases. The electronic sensitisation induced in SnO₂ by dispersed ruthenium seems to depend on the extent of electron transfer from the oxygen vacancies to ruthenium and then to O₂. The greater the transfer, the larger the electron deficient space-charge layer.

Introduction

It is well known that interaction with CO decreases the resistance of SnO₂, while reaction with O₂ increases it. For this reason, SnO₂ is widely used as the base material in gas sensor devices, the difference in electric properties between reducing and oxidising gases being enhanced by the presence of supported transition metals.¹

The most widely accepted explanation for the varying sensitivity of SnO₂ (the ratio of the resistance in air to that in a gas containing an inflammable component)² in different atmospheres was that negatively charged oxygen adsorbates (O₂⁻, O⁻, O²⁻) cover the surface of the semiconductive oxide in air and cause an electron depleted surface layer; while inflammable gases, like H₂, CO, CH₄, consume oxygen adsorbates, any trapped electrons returning to the oxide.¹

More recently, a very different explanation was given for SnO₂ thin film sensitivity, it being suggested³ that the resistivity changes due to exposure to reducing or oxidising gases are caused more by changes in surface defect density (oxygen vacancies and Sn²⁺ centres) rather than by variation of the oxygen chemisorbed species.

Our spectroscopic and spectromagnetic studies on the reactivity of SnO₂, prepared by the sol-gel condensation method with combustible (H₂, CO) gases and air,^{4,5} are in agreement with this. We demonstrated that singly ionised oxygen vacancies (V_O⁺) and tin defects (Sn²⁺) are present in SnO₂ treated with CO reducing gas; both defects interact with

O₂ and reduce it to O₂⁻ and O²⁻, depending on the treatment temperature.⁵

As for the sensitising effect of transition metal centres, it has been suggested^{1,2} that it is the consumption of oxygen adsorbates on the metal plus those on the SnO₂ surface that enhances the oxide sensitivity. Given that SnO₂ defects are believed to vary conduction properties, questions arise about the role of the same defects^{4,5} when transition metal centres are present. Do the V_O⁺ remain stable? Can they transfer electrons to Sn⁴⁺ and, when exposed to air, reduce molecular oxygen? Do they have any role in SnO₂ electronic sensitisation?⁴

The promoting effect of transition metals depends not only on the type and amount of the metal but also on the electronic interaction between metal and semiconductor. As a consequence the dispersion of the metal on the SnO₂ surface and the different methods of loading the metal are critical to the electrical properties.^{1,2}

The present paper reports the preparation and electron paramagnetic resonance (EPR) characterisation of ruthenium-dispersed SnO₂ samples, obtained either by impregnation of SnO₂ with the transition metal precursor, tris(acetylacetonate)ruthenium(III) [Ru(acac)₃], or by cogelation of the tin oxide precursor, tetra(*tert*-butoxy)tin(IV) [Sn(OBu^t)₄], and the ruthenium oxide precursor, [Ru(acac)₃]. The electron paramagnetic resonance investigation also considered sample reactivity with oxidising and reducing gases, in order to compare the chemical response of material prepared by two different methods of metal loading.

Our hypotheses concerning the origin of electronic sensitisation¹ were prompted by the variation in the number of paramagnetic oxygen vacancies and the change in the oxidation state of the loaded metal when Ru–SnO₂ interacted with inert (Ar) and combustible (CO) gases, and air.

Experimental

Preparation of ruthenium-dispersed SnO₂ samples by the sol-gel method

Tris(acetylacetonate)ruthenium(III)-dispersed tin oxide {[Ru(acac)₃]-SnO₂}. A tris(acetylacetonate)ruthenium(III) [Ru(acac)₃] (0.07539 g) solution in 50 ml of ethanol–acetylacetone, 4:1 v/v mixture, was prepared; 6 g of tetra(*tert*-butoxy)tin(IV) [Sn(OBu^t)₄]⁶ was dissolved, under inert atmosphere, in 12 ml of absolute anhydrous ethanol and the solution added to 30 ml of the [Ru(acac)₃] solution, under stirring. After a few minutes, 10 ml of an ethanol–water solution 4:1 v/v was added. Sol-gel transition occurred within 2–3 d at room temperature, giving a homogeneous purple gel. This gel, dried under vacuum at room temperature, gave a high surface area powder (100 m² g⁻¹), the xerogel.

Ruthenium-dispersed tin oxide (Ru–SnO₂). This was obtained by thermal treatment of the powdered [Ru(acac)₃]-SnO₂ xerogel at 673 K for 4 h in an air stream (100 cm³ min⁻¹). The surface area decreased significantly to 50 m² g⁻¹. Elimination of the acetylacetonate ligand was monitored by infrared spectroscopy in the region of the acetylacetonate vibrational modes. At 473 K the symmetric and antisymmetric vibrational carboxylate modes of the acetylacetonate ligand (1600–1400 cm⁻¹) disappeared (Fig. 1A).

The samples contained 0.5% (w/w) of Ru, corresponding to a [Ru(acac₃)]/SnO₂ molar ratio of 0.8.

Preparation of ruthenium-dispersed SnO₂ samples by the impregnation method

Tris(acetylacetonate)ruthenium(III)-dispersed tin oxide {[Ru(acac)₃]-SnO₂}. Powdered SnO₂ (2 g), obtained according to ref. 5, was heated at 673 K for 4 h under flowing air (100 cm³ min⁻¹). A [Ru(acac)₃] solution in anhydrous deaerated *n*-pentane (10 mg in 15 ml) was then added dropwise to the powder under a stream of dry argon. When addition was complete, the mixture was dried at room temperature, still under a dry argon flow.

Ruthenium-dispersed tin oxide (Ru–SnO₂). This was obtained by thermal treatment of [Ru(acac)₃]-SnO₂ in an air stream (100 cm³ min⁻¹) for 4 h at 673 K. Surface area measurements performed after the treatment gave a value of 40 m² g⁻¹. The samples contained 0.4% (w/w) of Ru, corresponding to a [Ru(acac)₃]/SnO₂ molar ratio of 0.6.

Experimental procedures for spectroscopic measurements

The elemental analysis of ruthenium in both types of samples was performed by melting 50 mg of Ru–SnO₂, with 100 mg of KOH. The solid, at room temperature, was treated with a little water, evaporated, then heated to the melting point, again treated with a little water then transferred to a calibrated (50 ml) vessel to which a 5% HCl solution was added. After centrifugation, metal analysis was performed by Atomic Emission Inductively Coupled Plasma (ICP-AES) spectroscopy.

Electron paramagnetic resonance (EPR) measurements were performed on samples interacting with flowing gases in a quartz apparatus suitable for both gas flow and EPR measurements:

(i) Ru(acac)₃-SnO₂ powdered samples (≈0.5 g) were treated at 673 K for 4 h in a dry air stream (100 cm³ min⁻¹), providing Ru–SnO₂. The spectra were recorded before any gas treatment, as for the pure SnO₂ samples.⁵

(ii) Ru–SnO₂ underwent gas interaction using SIAD gases

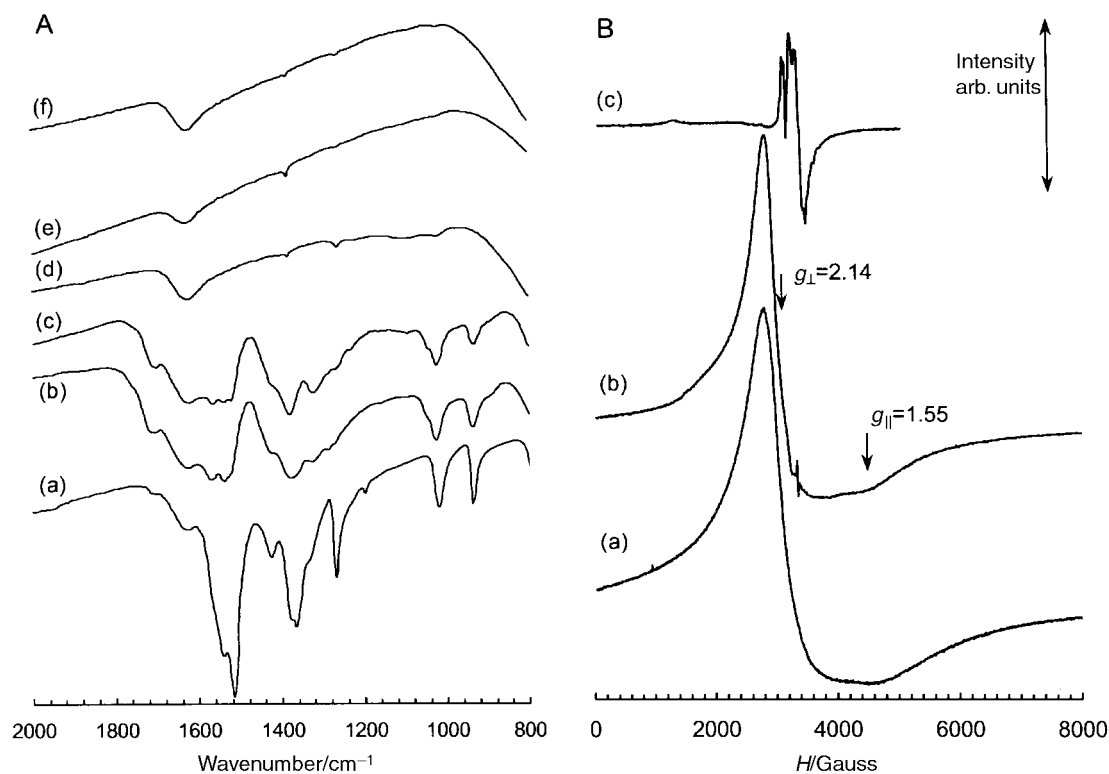


Fig. 1 (A) Infrared spectra of: (a) pure [Ru(acac)₃]; (b) [Ru(acac)₃]-SnO₂ xerogel; (c)–(f) sample (b) treated in air for 1 h at 373, 473, 573, 673 K. (B) EPR spectra, recorded at 123 K under an argon atmosphere, of: (a) a solution of [Ru(acac)₃] in acetylacetone (1% w/w); (b) [Ru(acac)₃]-SnO₂ xerogel; (c) sample (b) treated in air for 4 h at 673 K.

either pure (argon, air) or mixed [CO(0.5%)–argon]. The experimental procedure for the interaction required three steps:

(a) The gas was passed over the sample at room temperature and the flow rate ($100 \text{ cm}^3 \text{ min}^{-1}$) set within 5 min. The temperature was then increased by $50^\circ \text{C min}^{-1}$ up to the selected treatment temperature (typically 298, 373, 473, 573, 673 or 773 K). All the heating stages of the processes were performed in a dry atmosphere.

(b) Contact with flowing gases was maintained for 30 min at the selected temperatures.

(c) The samples were cooled rapidly (in about 5 min) to room temperature and their spectra recorded.

(iii) After each sample interaction with the appropriate gas, the sample was exposed to a dry air stream ($100 \text{ cm}^3 \text{ min}^{-1}$) for 10 min at room temperature to investigate its interaction with oxygen.

The EPR spectra were generally recorded at 123 K under the same atmosphere as the treatment. When air was present the spectra were taken after evacuating the air, in order to avoid line broadening due to a possible interaction with paramagnetic surface species. Such line broadening is well known, and is brought about by the magnetic interaction of O_2 with the surface paramagnetic species. Exchange interaction occurs, the effect being commonly called exchange broadening, and this allows the easy identification of surface or bulk paramagnetic species.

Apparatus

Electron paramagnetic resonance (EPR) spectra were recorded on powdered samples by a conventional Bruker EMX spectrometer, taking care that the sensitive region of the resonant cavity was always filled to the same extent. The g -values were measured by standardisation with diphenylpicrylhydrazyl (DPPH). The amounts of paramagnetic species were assessed by double integration of the resonance line areas, taking as the reference the area of the Bruker weak pitch ($9.7 \times 10^{12} \pm 5\% \text{ spin cm}^{-1}$). The ratio between the number of Ru^{3+} centres and the total amount of ruthenium was calculated by reference to the area of the Ru^{3+} resonances in the precursor $[\text{Ru}(\text{acac})_3]$ solution.

The resonance lines were simulated by the Bruker WIN EPR SimFonia program, taking as final g -tensor component values those giving the best fit with the experimental lines.

BET surface area measurements were performed on a Coulter SA 3100 instrument, after degassing samples at 303 K for 5 h.

Infrared spectra were recorded on a Jasco FT-IR 410 spectrophotometer, diluting samples in KBr.

Metal analyses were performed by (AES-ICP), on a Jobin-Yvon 38 AES-ICP spectrophotometer.

Results

Ruthenium-dispersed SnO_2 samples prepared by the sol–gel method

The EPR spectrum of the dried $[\text{Ru}(\text{acac})_3]\text{-SnO}_2$ xerogel is shown in Fig. 1B, line (b). The strong resonance lines, with axial symmetry, have an easily detectable perpendicular component at $g=2.14$ and a less evident parallel component at $g=1.55$, both similar to those in the spectrum of $[\text{Ru}(\text{acac})_3]$ in frozen acetylacetonate solution [Fig. 1B, line (a)]. The spectrum is characteristic of a low spin d^5 electronic configuration⁷ and confirms that the inclusion of $[\text{Ru}(\text{acac})_3]$ in the SnO_2 gel does not significantly modify the ligand field around ruthenium. The number of Ru(III) paramagnetic centres in the xerogel samples corresponded to all the $[\text{Ru}(\text{acac})_3]$ introduced into the sol precursor.

Thermal treatment of the xerogel at 673 K in an air stream

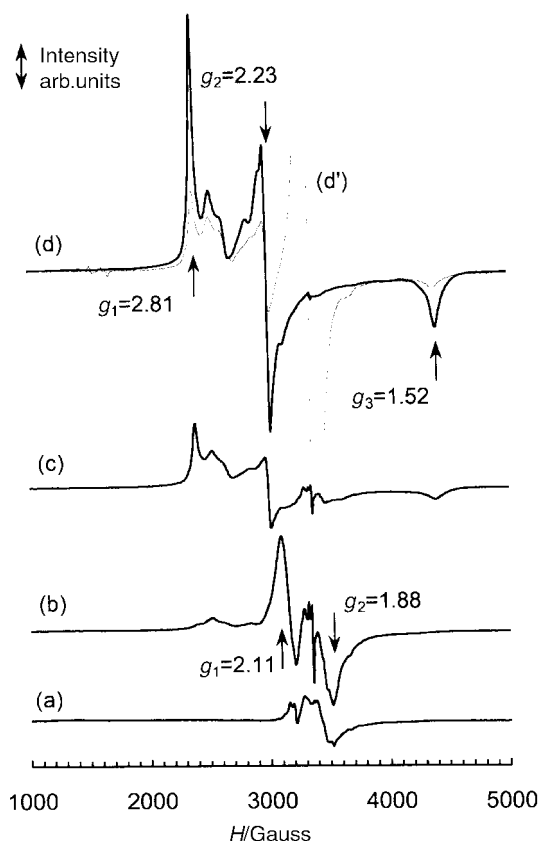


Fig. 2 EPR spectra, recorded at 123 K under an argon atmosphere, of: (a) $[\text{Ru}(\text{acac})_3]\text{-SnO}_2$ xerogel treated in air for 4 h at 673 K; (b)–(d) sample (a) treated with CO(0.5%)–Ar for 30 min at 273, 373 and 773 K. (d') sample (d) treated with air at room temperature for 10 min.

for 4 h led to strong modification of the spectrum. The resonance lines of $[\text{Ru}(\text{acac})_3]$ disappeared [Fig. 1B, line (c) and Fig. 2, line (a)] and several superimposed lines, corresponding to a very small percentage (about 3%) of the Ru^{3+} precursor centres, became evident in Ru-SnO_2 samples. The small amount of paramagnetic species, with respect to both the precursor $[\text{Ru}(\text{acac})_3]\text{-SnO}_2$ and, especially, the species generated further on (see later), caused us to limit the studies on identification.

Treatment with a dry CO(0.5%)–argon stream at increasing temperatures, 298–773 K, [Fig. 2 lines (b, c and d)] modifies the spectrum of the thermally air-treated xerogel, giving several resonances whose g_{av} values still lie in the region characteristic of low spin d^5 centres.⁷

It is well known that for a d^5 electronic configuration the equations giving the principal components of the g -tensor (see ref. 7 and references therein) predict large variations for the individual values, depending on the distortion of the surrounding crystal field and on the spin–orbit coupling contribution of the metal.⁸ The spectra of CO–argon-treated samples [Fig. 2 lines (b, c and d)] can be attributed to two different Ru^{3+} centres present in major amounts: $\text{Ru}^{3+}(\text{A})$ with $g_1(\text{A})=2.11$, $g_2(\text{A})=1.88$ and $\text{Ru}^{3+}(\text{B})$ with $g_1(\text{B})=2.81$, $g_2(\text{B})=2.23$, $g_3(\text{B})=1.52$. At 373 K the (A) species disappeared [Fig. 2 line (c)], species (B) becoming evident and predominating at all temperatures above this. The (A) species has g -component values similar to those of carbonyl Ru^{3+} derivatives,⁸ the g -component values of the (B) species are similar to those reported for Ru^{3+} in the field of oxide ligand O^{2-} .⁸ A deconvolution of the spectrum obtained after CO–argon treatment at 773 K (Fig. 3) showed that the species present in the spectra after treatment from 373 to 773 K are of three types: $\text{Ru}^{3+}(\text{B})$, the most abundant, with $g_1(\text{B})=2.811$, $g_2(\text{B})=2.234$, $g_3(\text{B})=1.523$; $\text{Ru}^{3+}(\text{C})$ with $g_1(\text{C})=2.655$,

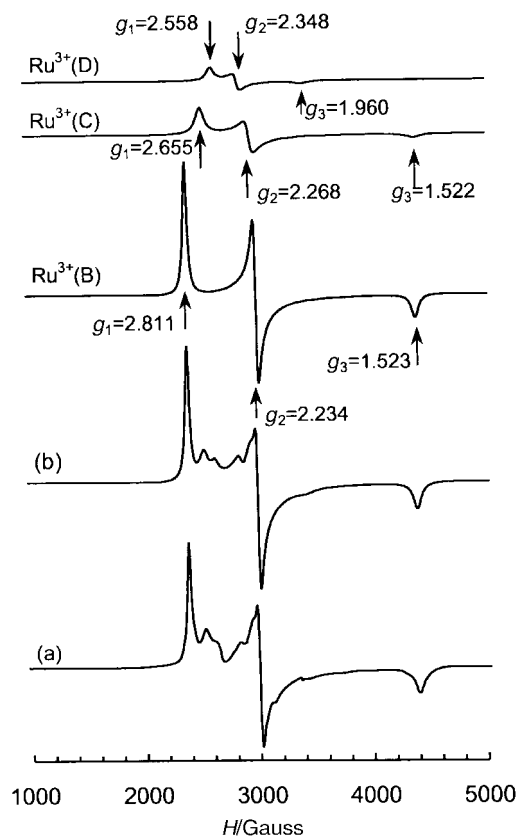


Fig. 3 EPR spectrum of Ru-SnO₂ obtained by the sol-gel process, treated with CO(0.5%)-Ar for 30 min at 773 K. (a) Experimental spectrum; (b) simulated spectrum. The simulated spectrum is the sum of the single species Ru³⁺(B), Ru³⁺(C) and Ru³⁺(D).

$g_2(C)=2.268$, $g_3(C)=1.522$; Ru³⁺(D) with $g_1(D)=2.558$, $g_2(D)=2.348$, $g_3(D)=1.960$. Both the C and D species could, in principle, be assigned to Ru³⁺ centres in the field of O²⁻ ligands, where the different anisotropy of the g -tensor with respect to B is more probably due to different ligand field symmetry and to the various spin-orbit coupling contributions of differently charged Ru³⁺ centres.

Fig. 4 shows the trend vs. CO-argon treatment temperature

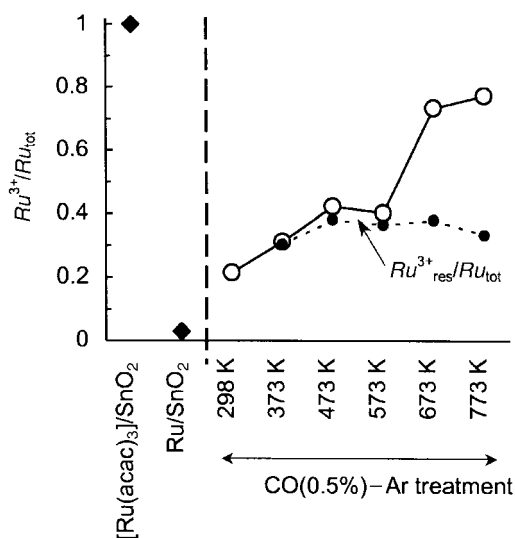


Fig. 4 Number of paramagnetic Ru³⁺ centres, as a fraction of the total amount of Ru in: (◆) [Ru(acac)₃]-SnO₂ xerogel and Ru-SnO₂; (○) Ru-SnO₂ treated with CO(0.5%)-Ar for 30 min at the indicated temperatures; (●) the same samples after a further treatment with air for 10 min at room temperature.

for the ratio of Ru³⁺ (all paramagnetic centres) to the total number of Ru centres, Ru^{3+}/Ru_{tot} . The same figure also reports Ru^{3+}/Ru_{tot} for [Ru(acac)₃]-SnO₂ xerogels and Ru-SnO₂ unreduced samples. The number of Ru³⁺ centres increases with temperature up to 773 K, where it corresponds to about 80% of the total ruthenium present in the original xerogel.

Subjecting the samples, previously reduced with dry CO(0.5%)-argon at 298–773 K, to a 10 min treatment with flowing air at room temperature, leads to the formation of Sn⁴⁺-O₂⁻ paramagnetic centres. These were identified by their characteristic EPR resonances ($g_1=2.019$, $g_2=2.001$, $g_3=1.996$)^{4,5} (Fig. 5, inset). The number of Sn⁴⁺-O₂⁻ paramagnetic centres increases with the temperature of CO-argon reduction (Fig. 5). Residual Ru³⁺ centres of type (B), (C) and (D), Ru^{3+}_{res} , were observed after air treatment. The ratio Ru^{3+}_{res}/Ru_{tot} is also reported in Fig. 4: at lower temperatures (298–573 K), very few Ru³⁺ centres interacted with oxygen, whereas at 673 and 773 K a great number did, giving a correspondingly high number of Sn⁴⁺-O₂⁻ centres. Ru³⁺(A) centres do not react with oxygen; the Ru³⁺(B), Ru³⁺(C) and Ru³⁺(D) centres react to a different extent, e.g. in samples previously reduced at 773 K, the number of Ru³⁺(B) centres decreases by about 80% after air treatment, while the proportion of Ru³⁺(C) and (D) centres dropped to about 50%, suggesting that the Ru³⁺(B) centres probably lie more towards the surface [Fig. 2 lines (d) and (d')]. Reduction treatment at $T > 573$ K probably pushed both the Ru³⁺(B) and Ru³⁺(C) centres towards the surface where some fraction of them interacted with air at room temperature under the mild conditions used.

Ruthenium-dispersed SnO₂ samples prepared by impregnation method

Fig. 6 shows the EPR spectra of [Ru(acac)₃]-SnO₂ samples obtained by impregnation of SnO₂ with [Ru(acac)₃] that underwent the same treatment as the sol-gel samples. Some of the resonance lines are similar to those for similarly treated sol-gel samples. For [Ru(acac)₃]-SnO₂ samples [Fig. 6 line (a)], the lines of [Ru(acac)₃] were observed; well overlapped resonances

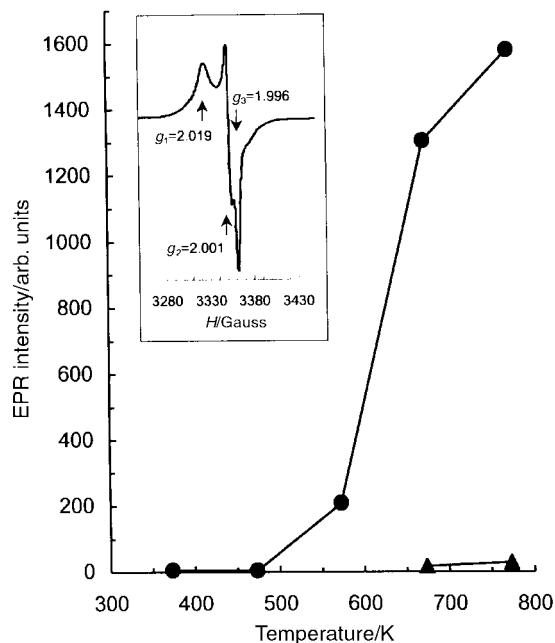


Fig. 5 Amount of Sn⁴⁺-O₂⁻ after treatment with CO(0.5%)-Ar 30 min at the indicated temperatures and further treatment with air 10 min at room temperature in (●) Ru-SnO₂ obtained by the sol-gel process and (▲) Ru-SnO₂ obtained by impregnation. Inset: EPR spectrum of Sn⁴⁺-O₂⁻.

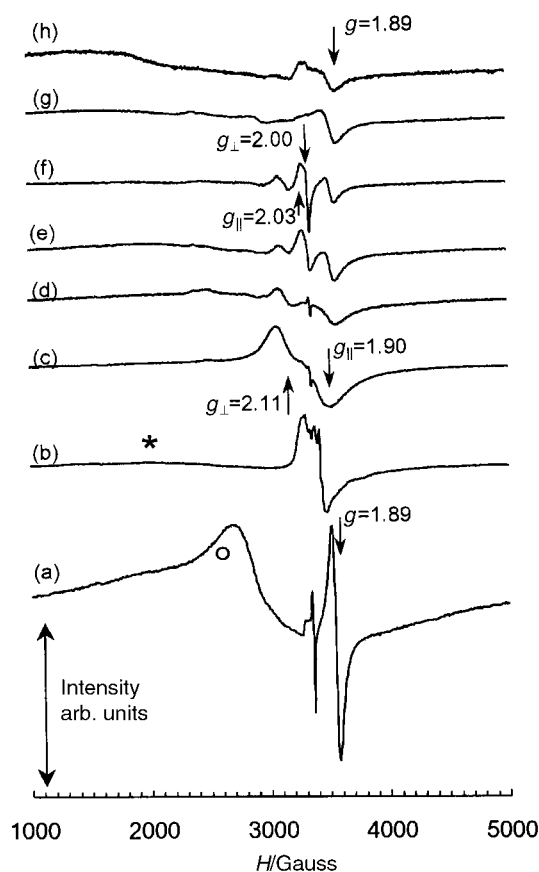


Fig. 6 EPR spectra, recorded at 123 K under argon atmosphere, of: (a) [Ru(acac)₃]-SnO₂ obtained by impregnation. ° Indicates the signal of [Ru(acac)₃]; (b) sample (a) treated in air for 4 h at 673 K. * Indicates the broad signal due to clusters of metal centres; (c)–(h) sample (b) treated with CO(0.5%)-Ar for 30 min at 273, 373, 473, 573, 673 and 773 K.

of low intensity (about 3% of the total ruthenium) were detectable after air treatment at 673 K in the spectrum of Ru-SnO₂ [Fig. 6 line (b)]. Lines due to Ru³⁺ (A) were detected for samples treated with CO(0.5%)-argon at 298–573 K (Fig. 6 lines (c–f)) and the Ru³⁺ stability was higher than in sol-gel samples, though the amount was very small; only traces of the Ru³⁺ (B) species were evident and there were no Ru³⁺ (C) or Ru³⁺ (D) centres. The absence of Ru³⁺ (C) and Ru³⁺ (D) centres, which in sol-gel samples were less reactive to O₂ than Ru³⁺ (B), confirms that they probably lie in a subsurface or bulk region.

A new axial species, having $g_{\parallel}=2.03$, $g_{\perp}=2.00$, appeared for samples reduced at 473–573 K. The sharpness of the resonances and the g -component values⁸ suggested they were due to Ru(i) carbonyl derivatives.

All the resonances found for the CO-argon reduced samples, and attributable to magnetically-diluted ruthenium species, are of lower intensity (very low percentage of the total ruthenium) than those in the sol-gel samples and disappear after reduction at 773 K.

Very broad resonances (about 10% of the total ruthenium), probably due to clusters of metal centres, are detectable after reduction at all temperatures.

Signals attributable to V_O⁺ centres ($g=1.89$) were observed in the spectra of freshly impregnated samples [Fig. 6 line (a)] but were still evident after reduction at 473 K and disappeared after treatment at 673 K in air [Fig. 6 line (b)].

Samples reduced by CO-argon from rt to 573 K gave an amount of Sn⁴⁺-O₂⁻ which was below detection limits, when reacted with air at room temperature; also, at 673 and 773 K

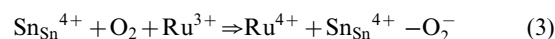
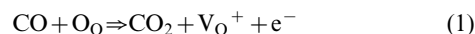
the number of Sn⁴⁺-O₂⁻ centres was very small compared with the sol-gel samples (Fig. 5).

Discussion

The aim of the discussion is to compare the behaviour of Ru-SnO₂, obtained by cogelation of [Sn(OBu')₄] and [Ru(acac)₃] metal precursors, with that of Ru-SnO₂ obtained by impregnating SnO₂ with a [Ru(acac)₃] precursor solution.

The EPR results show that the Ru³⁺ paramagnetic centres [Ru(acac)₃] present in the dried xerogel are mostly oxidised to Ru⁴⁺ by thermal treatment in air at 673 K for 4 h. Reduction under CO(0.5%)-argon atmosphere, progressively increasing the treatment temperature, leads to the formation of four different types of Ru³⁺ centre and electron injection by CO leads to increasing reduction of the Ru⁴⁺ centres to Ru³⁺. The Ru^{3+}/Ru_{tot} ratio, evaluated to be about 0.8 after reduction at 773 K, excluded that ruthenium assumed oxidation states lower than trivalent. This suggests that in samples obtained by cogelation, the metal centres remain well dispersed in the matrix of oxide anions. The metal centres tend to assume a high oxidation state as isolated ions rather than form clusters of metal centres in a more reduced electronic state. Thus, all the Ru³⁺ centres present in the xerogel react with O₂ during air treatment at 673 K to give Ru⁴⁺ centres; all the Ru³⁺ centres can be regenerated if the oxidised sample is treated with CO-argon at 773 K. It appears that the cogelation procedure allows interaction of the metal centres in the subsurface or bulk regions with the surrounding atmosphere, as occurs at the surface.

Singly ionised oxygen vacancies, observed on treating pure SnO₂ with CO(0.5%)-argon atmosphere⁵ were absent. An explanation for this could be that in the presence of a well dispersed metal, the V_O⁺ defects, formed by interaction of CO with SnO₂, transfer all their electrons to Ru⁴⁺ centres; such a transfer could occur due to the lower energy of the metal Fermi level with respect to SnO₂ and to a very efficient metal-semiconductor contact in sol-gel samples. It is probable that a great many Ru⁴⁺ centres could substitute Sn⁴⁺ in samples prepared by cogelation, allowing a very efficient electron transfer mechanism. Such samples will, from now on, be referred to as ion-exchanged SnO₂ samples. Mild air treatment of Ru-exchanged SnO₂, previously reduced by CO(0.5%)-argon, causes the reduction of oxygen to the superoxide anion (Fig. 5), and residual Ru³⁺ centres are detectable (Fig. 4). There was no evidence of a ruthenium generated superoxide anion. The following sequence of reactions can be hypothesised:



The formation of Sn_{Sn}⁴⁺-O₂⁻ appears to be relevant in samples reduced at 673 and 773 K, where there was also a relevant decrease in the number of Ru³⁺ centres due to their oxidation to diamagnetic Ru⁴⁺ centres. Ru³⁺ (B), Ru³⁺ (C) and Ru³⁺ (D) centres present in reduced sol-gel samples may react with O₂ under mild oxidative conditions at room temperature. However, the number of Ru³⁺ (B) centres undergoes the largest decrease, probably because they lie near the surface. On comparing Ru-exchanged SnO₂ samples with the impregnated samples, it was observed that the impregnation process produced V_O⁺ oxygen defects, probably due to the transfer of lattice oxygens to the impregnating solvent (*n*-pentane). These defects, filled by the thermal treatment under air, do not affect the CO-argon reductions.

After treatment with CO-argon it seems that oxidation states

lower than +3 become stable: in fact the very low number of Ru^{3+} centres observed after reducing treatments, the presence of Ru^+ centres detected after reduction at 673 K and the broad resonances, found after all the reduction treatments, suggest that strong metal-metal interactions arise in impregnated samples, forming clusters of reduced metal centres.

No relationship was found in the impregnated samples for the number of Ru^{n+} and $\text{Ru}^{(n-1)+}$ centres before and after reduction.

Paramagnetic oxygen vacancies were evident after treating the impregnated samples above 473 K; this suggests that semiconductor-metal contact is less intimate in the impregnated samples than in the sol-gel, hindering easy electron transfer from V_O^+ centres to the metal.

Finally, the amount of $\text{Sn}_\text{Sn}^{4+}\text{-O}_2^-$ in impregnated samples is very small and much lower than in the sol-gel samples.

Conclusions

The sol-gel method of dispersing a metal in SnO_2 avoids the risk that oxygen vacancies will occur through oxidation of the impregnating solvent.

Transition metal-dispersed SnO_2 samples obtained by cogelation of metal precursors contain a controlled amount of dispersed and reactive metal centres in oxidised electronic states.

The absence of clustering and ligand molecules (CO) around the metal after exposure to a CO-argon reducing atmosphere, makes the metal-semiconductor contact more intimate than in impregnated samples.

No singly ionised oxygen vacancies were observed after reduction of sol-gel samples with CO-argon. Unlike in impregnated samples, all the electrons are transferred to the metal centres due to the more intimate metal-semiconductor contact. Thus, in the ion-exchanged SnO_2 samples, the electron exchange processes with the surrounding atmosphere involve only two oxidation states of the transition metal.

On the basis of previous arguments, two main conclusions can be drawn:

It can be expected that the ion-exchanged SnO_2 samples

described could, owing to their high reactivity towards the surrounding atmosphere and the possibility of controlling the number of centres active in the redox process, be more appropriate materials than the metal-impregnated samples for use in CO gas sensor devices.

The formation of oxygen defects, V_O^+ , under reducing treatment and the transfer of electrons from V_O^+ to the metal have been confirmed as being essential to the sensitisation mechanism of metal-dispersed tin oxide. Furthermore, it appears, as has been suggested by recent SnO_2 thin film literature, that the key factor in sensitisation by transition metals is more the variation in oxygen defects than variation in chemisorbed oxygen species.

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