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INTERACTIONS OF TIN OXIDE SURFACE WITH O_2, H_2O AND H_2

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Interactions of tin oxide surface with oxygen, water vapor, and hydrogen have been investigated. Temperature programmed desorption (TPD) chromatograms of oxygen showed the formation of four kinds of oxygen species on SnO_2 which were desorbed around 80°C (α_1), 150°C (α_2), 560°C (β), and above 600°C (γ), respectively, on heating at 20°C/min. Based on electric conductivity and ESR measurements, these species were assigned as O_2 (α_1), O_2^- (α_2), O^- or O^{2-} (β), and a part of lattice oxygen (γ), respectively. Two types of water adsorption were indicated by broad TPD peaks centered at 100°C (α) and 400°C (β), for which molecular and dissociative (surface hydroxyls) adsorbates were assigned respectively. Of these, β caused an increase in electric conductivity of SnO_2. The interactions of H_2 with SnO_2 surface were complicated by the reduction of SnO_2 taking place at higher temperature. Exposure of evacuated SnO_2 to H_2 at room temperature gave a large TPD peak centered at 100°C (α). After cooling in H_2 from 200°C to room temperature, however, large amounts of H_2O desorption were observed, in addition to the H_2 desorptions around 100°C (α) and 220°C (β). The type α was shown to be of depletive type. These phenomena are discussed briefly in relation to the actual case of gas detection.

1. Introduction

It is well-known that the electric conductivity of a metal oxide changes as a result of interactions with several gases. This phenomenon was first applied for the detection of inflammable gases in 1962 by Seiyama et al. [1]. The development of gas detectors (or sensors) using metal oxide semiconductors was much enhanced by the finding of Loh [2] and Shavor [3] that the response and sensitivity of gas detection were greatly improved by the addition of small amounts of noble metals such as Pt and Pd to metal oxides. Since then various types of gas sensors for inflammable gases have been developed mainly by use of SnO_2 and ZnO_2. However, the nature of the gas–solid interactions involved has not been well understood. This paper deals with the interactions of SnO_2 surface with oxygen, water vapor, and hydrogen gases. These gases are the components which are involved in the detection of hydrogen gas leakage in air. We have so far studied oxygen adsorption on several metal oxides by means of a temperature programmed desorption (TPD) technique

[4,5], and found that the technique is very useful for such studies. In this study, the adsorption of gases on SnO_2 powder was first studied under various conditions by means of the TPD technique. It was then attempted to elucidate the effects of specific types of adsorption on the electric conductivity of SnO_2.

2. Experimental

Tin oxide, SnO_2 (rutile type), was prepared by treating metallic tin (five nine) with heated nitric acid. The precipitate (β-stannic acid) obtained was washed with water, dried at 100°C, and calcined at 600°C for 10 h in air. The powder was pressed and ground to granules of 20–60 mesh for use. The surface area was measured by BET method before and after use.

The TPD experiments were performed as described elsewhere [4]. The fresh sample (1 g) was loaded in the apparatus and evacuated ($\sim 10^{-4}$ Torr) at 600 or 700°C for several hours. A routine TPD experiment consisted of sample conditioning, gas adsorption, and temperature programmed desorption. For sample conditioning the sample was exposed to 100 Torr of oxygen for 30 min at 600 or 700°C followed by evacuation for 30 min at the same temperature. Then the sample was cooled to the desired temperature (T°C) in vacuo, at which time O_2, H_2O or H_2 was introduced to pressures adequate for the gas adsorption. The subsequent manipulations were performed in two ways, i.e. the sample was either cooled to room temperature (RT) at ca. 10°C/min followed by evacuation for 15 min (Procedure I), or kept standing for 30 min followed by evacuation at the same temperature and cooling to RT in vacuo (Procedure II). These adsorption procedures will be expressed hereafter as Ad.I (T°C → RT) and Ad.II (T°C). The thermal desorption was carried out in a helium or nitrogen flow (30 cm^3/min) at a heating rate 20°C/min unless noted otherwise. The desorbed gas was monitored with a thermal conductivity detector. In the case of H_2 adsorption on SnO_2, desorbed gases were H_2 and/or H_2O. H_2 was monitored in a nitrogen flow, with a dry ice trap before the detector to condense H_2O. H_2O was monitored in a helium flow without separating H_2.

The electric conductivity was measured in a separate cell. The granules of SnO_2 (ca. 0.5 g) were loaded between two electrodes (gold plates) in a quartz tube (0.9 mm in diameter) which was electrically connected with a resistor (variable) in series. By applying a direct current, the voltage drop between the electrodes was continuously measured. In some cases, SnO_2 powder was pressed into a disc 2 mm thick, on one side of which gold ribbon electrodes were placed 3 mm apart. The relative changes of conductance obtained by the latter method agreed well with those obtained by the former method. The gas adsorption was manipulated almost in the same way as in the TPD experiments, but the thermal desorption was carried out in vacuo ($\sim 10^{-4}$ Torr) in these measurements.

3. Results and discussion

3.1. Interactions with oxygen

The TPD spectra of oxygen observed under various conditions are shown in fig. 1. Desorption (or adsorption) phenomena were greatly affected by the adsorption method or the state of SnO_2. After evacuation at 700°C followed by oxygen adsorption by Ad.II (RT), only a desorption peak (α) appeared around 100°C (curve 1). After Ad.I (150°C → RT), however, this peak was split into two peaks centered at 80°C (α_1) and at 150°C (α_2) (curve 2). On the other hand, oxygen adsorption at higher temperature gave entirely different results. Curves 3 to 8 were obtained after Ad.II (400°C) at various pressures of oxygen. The curves show desorption peaks (β) at ca. 500°C and ascents (γ) above 600°C. It is noted that the β peaks are sensitive functions of the oxygen adsorption pressure but the ascents are relatively insensitive. This suggests that β desorption is ascribed to certain oxygen species adsorbed on SnO_2 while γ is likely to be the dissociation of a part of lattice oxygen. Taking into account that γ desorption does not appear after low temperature adsorption following the preevacuation at 700°C, it is considered that the preevacuated SnO_2 recovers the oxygen deficiency during the high temperature adsorption and dissociates it as γ desorption on heating.

As mentioned above, oxygen is adsorbed on SnO_2 in at least three states, α_1, α_2 and β. It was attempted to assign these adsorbates by ESR measurements. For this purpose, the sample was packed in a thin quartz tube and subjected to the same treatments as in the TPD experiments. It was found that the oxygen adsorption by

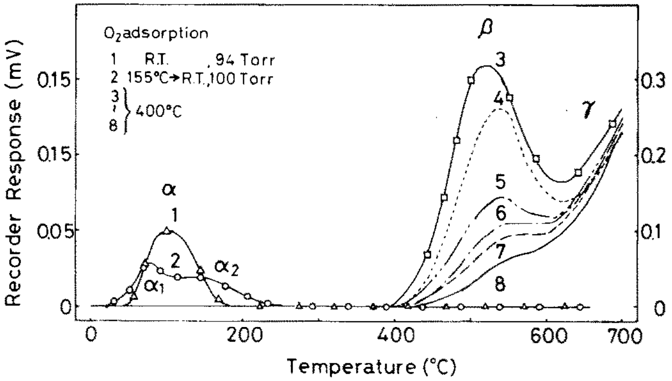

Fig. 1. TPD chromatograms of oxygen after oxygen adsorption under various conditions. The adsorption temperatures and pressures are indicated in the figure. The adsorption pressures for curves 3 to 8 are 99, 48, 16, 6, 3, and 2 Torr, respectively. The heating rate for curves 3 to 8 is 10°C/min.

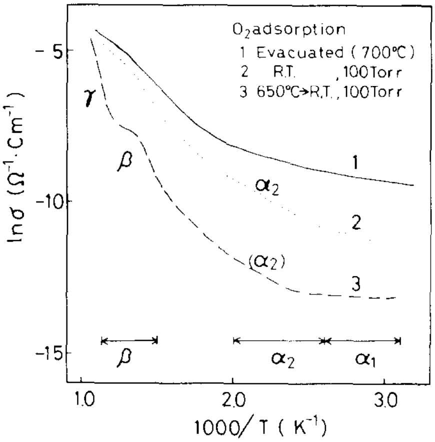

Fig. 2. Changes in the electric conductivity of SnO_2 on heating after evacuation at 700°C (curve 1), and after oxygen adsorption by Ad.II (RT) or Ad.I (650°C → RT) (2 and 3).

Ad.II (RT) gave an ESR spectrum at room temperature. The spectrum has anisotropic g values of $g_1 = 2.025, g_2 = 2.008$ and $g_3 = 2.002$ which are in fair agreement with the reported data [9] for O_2^- on SnO_2. In order to seek the correlation of the signal with the TPD spectra, the signal intensity was measured repeatedly after raising sample temperature stepwise at 20°C intervals in vacuo. As a result, the intensity was found to decrease over a wide temperature range of 60–300°C but the most rapid and significant decrease was observed between 100 and 200°C, a temperature range which coincides very well with that of the desorption peak α_2. On the basis of these results, the α_2 adsorbates were assigned to O_2^- ions. This leads us further to assign the α_1 species, which are weaker adsorbates than α_2, neutral O_2. As for β adsorbates, no information was collected by ESR. Considering the high desorption temperature of β, however, it seems reasonable to assign it to O^- or O^{2-}.

It is well known that the electric conductivity of SnO_2, σ, decreases extensively on exposure to oxygen. In order to know the effects of specific types of oxygen adsorption on σ separately, changes in σ were pursued under programmed heating conditions and compared with the previous TPD chromatograms. In this case, however, the thermal desorption was performed in vacuo. The results are shown in fig. 2. Curve 1 represents the standard relation of $\ln \sigma$ versus $1/T$ for a sample which was evacuated at 700°C but not subjected to further oxygen adsorption. With oxygen treatments of Ad.II (RT) and Ad.I (650°C → RT), the relation was modified into curves 2 and 3, respectively, being influenced by the thermal desorption of adsorbed oxygen or a part of lattice oxygen. The temperature ranges of respective types of thermal desorption are indicated at the bottom of the figure.

As mentioned earlier, α_1 and α_2 desorption appear in the case of Ad.II (RT). In the present measurements, the comparison of curve 2 with curve 1 (standard) indicates that a corresponding steep increase of σ appears only in the temperature range of α_2 desorption. This supports the previous assignment of α_1 (O_2) and α_2 (O_2^-), because only depletive type adsorbates can increase σ by desorption. In the higher temperature region, curve 2 goes almost parallel with curve 1. The changes of σ in that region probably reflects the intrinsic temperature dependences of σ free from the thermal desorption of adsorbates. After Ad.I (650°C → RT), on the other hand, two steep increases of σ appear in the higher temperature region, and they can be ascribed to β and γ desorptions by comparison with the TPD chromatograms. This shows that β and γ adsorbates are of depletive types as expected. In addition, however, curve 3 shows a considerable increase of ln σ in the temperature range corresponding to α_2 desorption. It is suggested that very minor amounts of α_2 adsorbates are formed even under such conditions though they are not detectable in the TPD chromatograms.

3.2. Interactions with water vapor

The TPD chromatograms of water vapor are shown in fig. 3a. After adsorption by Ad.I (600°C → RT), two large desorption peaks, α and β, appeared around 100 and 400°C, respectively. Adsorption by Ad.II (RT) gave almost the same result,

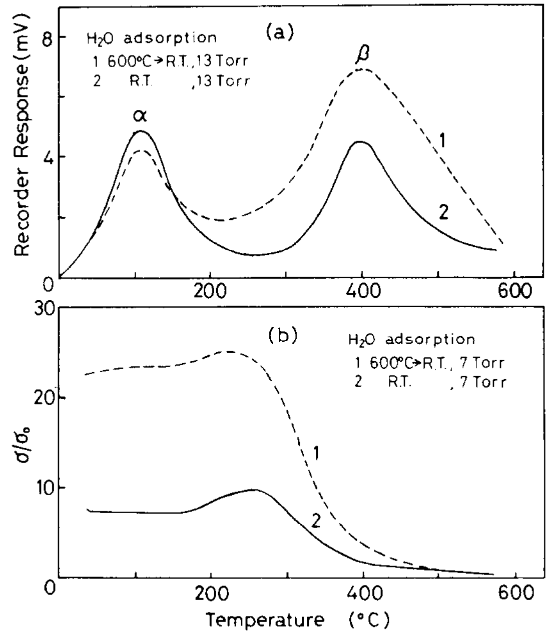

Fig. 3. Thermal desorption of water vapor (a), and the effects of water adsorption on the electric conductivity (b); σ_0 denotes the electric conductivity of an evacuated sample.

except that α grew a little, while β decreased. These results show that H_2O is adsorbed in two states. Harrison and Thornton [10] studied the adsorption of H_2O on SnO_2 by using IR spectroscopy. They found that molecular adsorbates are entirely desorbed by evacuation at 150°C, while surface hydroxyl groups are slowly desorbed beginning at 250°C but are not entirely desorbed even after evacuation at 500°C. Based on their results, α and β in the present case are ascribed to the desorption of molecular adsorbates and surface hydroxyl groups, respectively.

Adsorption of water vapor always produced a large increase in electric conductivity of SnO_2. The changes of σ under programmed heating are shown in fig. 3b, where σ is expressed relative to the conductivity (σ_0) of the same sample without H_2O adsorption. On heating, a large and rapid decrease in σ/σ_0 is observed in the temperature range of β desorption. It is therefore concluded that β adsorption of H_2O increases the electric conductivity of SnO_2 but α shows little influence on it.

3.3. Interactions with H_2

Interactions of the SnO_2 surface with H_2 were complex because the surface of SnO_2 was reduced with H_2 even at moderate temperatures. Adsorption of H_2 at room temperature, Ad.II (RT), gave a large TPD peak (α) centered at 100°C, while Ad.I (200°C → RT) gave two relatively small desorption peaks at 100°C (α) and 220°C (β), as illustrated by curves 1 and 2 in fig. 4a. In the latter case, it was found that a large amount of water vapor was also desorbed from the sample on heating (curve 3), which was confirmed by gas chromatography. The desorption temperatures, 100 and 400°C, coincided well with those observed in the TPD experiments of H_2O. This fact indicates that, by Ad.I (200°C → RT), H_2 is largely adsorbed as irreversible adsorbates which are desorbed as H_2O on heating, or, in other words, a large part of adsorbed H_2 is used to reduce SnO_2 to metal excess SnO_2.

The effects of H_2 adsorption on the electric conductivity of SnO_2 were also complicated by the occurrence of such reductive adsorption. Fig. 5 shows changes in σ with the admission of H_2 followed by evacuation. The phenomena were dependent on temperature. At room temperature, σ decreased rapidly to a steady value on admission of H_2 but it was hardly recovered to its initial value by the subsequent evacuation. This shows that the adsorption is very rapid but the desorption is slow at room temperature. At 85, 140 and 210°C, however, σ decreased immediately after the admission of H_2 and then increased slowly. The subsequent evacuation increased σ at 85 and 140°C but decreased σ at 210°C. At 270°C, the decrease in σ was no longer observed on admission of H_2. These phenomena are understandable if two types of adsorption are assumed, a type which takes place at lower temperature accompanying a fast decrease in σ and another which takes place more favorably at higher temperature causing an increase in σ. It is shown below that the former type corresponds to α adsorption while the latter is due mainly to the reductive adsorption previously mentioned.

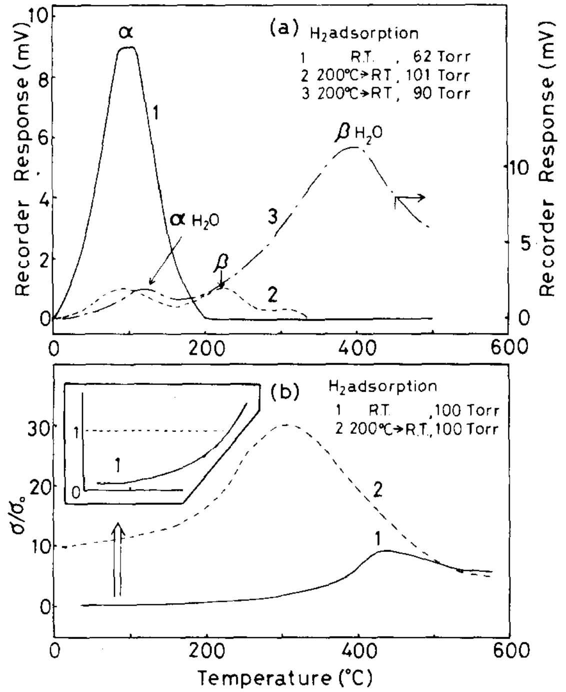

Fig. 4. (a) Thermal desorption of H_2 (curves 1 and 2) and H_2O (curve 3) after H_2 adsorption. (b) Changes in electric conductivity of SnO_2 on heating under the similar conditions.

The changes of the conductivity of H_2 adsorbed SnO_2 under programmed heating are shown in fig. 4b. Again the results are presented in terms of σ/σ_0 where σ_0 has the same meaning as before. In curve 1 obtained after Ad.I (RT), σ/σ_0 increases from 0.2 at room temperature to unity at ca. 200°C. This corresponds fairly well with the fact that α desorption takes place in the same temperature range. The changes of σ in the higher temperature region are not well characterized, but supposedly arise from the slow reduction of SnO_2 with part of the hydrogen still remaining on the surface and the subsequent desorption of the produced H_2O. On the other hand, the sample with Ad.I (200°C → RT) shows σ/σ_0 far exceeding unity already at room temperature. This is considered to be mainly due to the reduction of SnO_2. On heating the sample, σ/σ_0 shows a large maximum. The ascending part may arise from the further progress of reduction of SnO_2 with adsorbed H_2 while the descending part above 300°C can be ascribed to the desorption of the produced water. Because of the drastic nature of such reductive adsorption, the effects of β adsorption on the electric conductivity could not be observed.

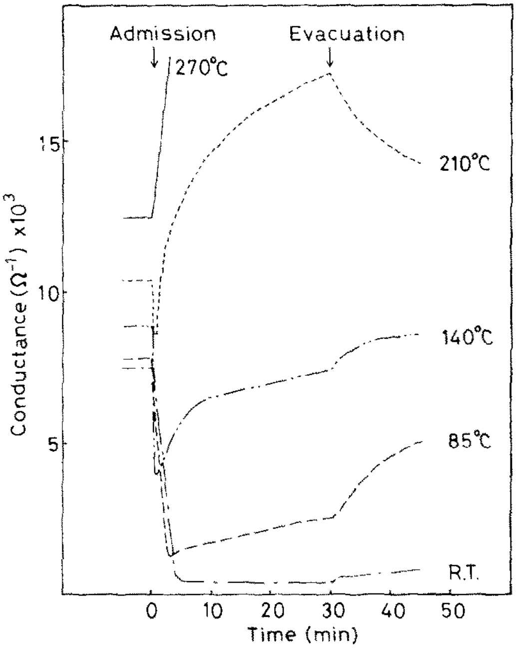

Fig. 5. Changes in conductance of a SnO_2 sample (disc) on introduction of H_2 and subsequent evacuation at various temperatures.

3.4. The types and amounts of adsorption

Table 1 summarizes the results on the adsorption of O_2, H_2O, and H_2 on SnO_2. The amounts of adsorption were estimated from the area under TPD peaks. The surface coverage, θ, in this case is defined as the number of adsorbed molecules of O_2, H_2O, or H_2 per surface tin atom and the value was estimated assuming that all the surface of SnO_2 was covered with {110} planes.

As shown in the table, θ for O_2 adsorption is very small, as usually experienced in metal oxide–O_2 systems [4]. This suggests that only surface defects of some sorts serve as the adsorption sites. It should be emphasized that, of the three adsorption types, α_1 (O_2) and α_2 (O_2^-) arise from low temperature adsorption after sample evacuation at a high temperature. Many workers have been pointed out that the formation of O_2^- is associated with the electron donor centers. In this sense, the evacuation at high temperature increases the electron donors needed to produce molecular adsorbates O_2^-. However, since it increases the neuteal type adsorbates as well, the high temperature evacuation also produces certain types of specific adsorption sites. In contrast, β adsorption was little affected by the sample conditioning. It is interesting to note that, from the viewpoint of the effect on the

Table 1
Adsorption of O_2, H_2O, and H_2 on SnO_2

Gas	Type (T_M) [a]	Species	$\Delta\sigma$ [b]	Adsorbed amounts (θ) [c] ($\times 10^{-8}$ mol/m^2) (%)	Adsorption conditions
O_2	α_1 (80°C)	O_2	0	0.32 (0.021)	155°C → RT, 100 Torr
	α_2 (150°C)	O_2^-	–	0.35 (0.022)	155°C → RT, 100 Torr
	β (520°C)	O^- or O^{2-}	–	12.4 (0.79)	400°C, 99 Torr
	γ (>600°C)	Lattice oxygen	–	6.3 (0.40) (<700°C)	400°C, 2 Torr
H_2O	α (110°C)	H_2O	~0	70.1 (4.5)	600°C → RT, 13 Torr
				79.9 (5.1)	RT, 13 Torr
	β (400°C)	–OH	+	231 (15)	600°C → RT, 13 Torr
				117 (7.5)	RT, 13 Torr
H_2	α (100°C)	–OH –SnH	–	14.7 (0.94)	RT, 90 Torr
				1.9 (0.12)	200°C → RT, 101 Torr
	β (220°C)	?	?	1.2 (0.07)	200°C → RT, 101 Torr
	Irreversible	–OH (H_2O)	+	25.4 (1.64) (as α-H_2O) 334 (21.5) (as β-H_2O)	200°C → RT, 62 Torr

[a] T_M means the temperature of desorption maximum.
[b] Changes of electric conductivity with the adsorption.
[c] θ means surface coverage (see text).

electric conductivity, β and γ are more important than α_1 or α_2.

The situation is different in the adsorption of H_2O. In the case of β adsorbates assigned to surface hydroxyls, θ reaches 15% after Ad.II (600°C → RT). If one consideres that a H_2O molecule produces two hydroxyls on adsorption, the real surface coverage may be twice of that. Weak molecular adsorbates (α) are also formed in comparable amounts. In addition to this, it was found in this study that the adsorption of β type adsorbates causes a large increase in σ. This is an interesting fact but the reason is not clear.

As mentioned before, the adsorption of H_2 on SnO_2 above 100°C forms largely irreversible adsorbates which are desorbed as H_2O on heating. Such reductive adsorption makes the largest contributions to the increases in σ on exposure to H_2 at moderate temperatures. On the other hand, adsorption at room temperature forms α species almost exclusively. Interestingly, this species is of a depletive type. For H_2 adsorption on ZnO at temperatures below 100°C, Eischens et al. [11] reported the hydride formation due to the heterolytic dissociation of H_2 as follows, $ZnO + H_2 \rightarrow OH + ZnH$. We consider that such hydride formation is also conceivable in the present case. However, the electric conductivity of SnO_2 decreases with adsorption while that of ZnO reportedly does not. Such a difference needs further study.

Finally, we refer briefly to the actual case of gas detection using SnO_2 sensors. A survey of table 1 is enough to show that actual phenomena taking place on the surface of SnO_2 sensors are not simple even in the detection of H_2 in air. It seems hardly acceptable to treat the electric conductivity changes during gas detection with simple models based on mere reversible adsorption of H_2, since such types of adsorption (α and β) are in fact of minor importance. In actual gas detection, oxygen adsorbates are present on the initial surface of sensors. As a result of contact with H_2, there will occur, to a greater or lesser extent, the consumption of the adsorbed oxygen by the H_2 together with an irreversible or reductive adsorption of H_2 to form surface hydroxyls, which lead to the adsorption or desorption of the resulting H_2O. All of these have serious effects on the electric conductivity of SnO_2 with rather complex temperature dependences. When the sensor temperature is as high as 500°C, however, the adsorption of H_2O and H_2 is no longer significant. It is considered that the change of σ at such temperatures can be treated as resulting mainly from the consumption of adsorbed (and lattice) oxygen with H_2.

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