Relationship between ethanol gas sensitivity and surface catalytic property of tin oxide sensors modified with acidic or basic oxides

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Received 14 February 1999; accepted 15 March 1999

Abstract

A semiconductor gas sensor using SnO_2 was loaded with acidic or basic oxides (5 wt.%) to investigate ethanol-gas sensing properties and related catalytic properties. The sensitivity to ethanol gas at 300°C increased tremendously with an addition of a basic oxide (e.g., La_2O_3), while it hardly changed with that of an acidic oxide (WO_3). It turned out that the addition of the basic metal oxide to SnO_2 brought about enhancement of catalytic activity not only for the dehydrogenation of ethanol gas to CH_3CHO but also for the consecutive oxidation of CH_3CHO to CO_2. On the other hand, the acidic metal oxide enhanced only the dehydration reaction, showing even an adverse effect on the consecutive oxidation. Based on these results, it was concluded that the enhancement of the catalytic oxidation activity to an appropriate level could be a reason for the high sensitivity to ethanol gas for the sensors loaded with basic oxides, particularly one loaded with La_2O_3. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Semiconductor gas sensors that utilize semiconducting metal-oxides such as SnO_2 and ZnO were first proposed by Seiyama et al [1] and commercialized by Taguchi [2]. The sensors are currently used popularly for the detection of inflammable gases (CH_4, C_3H_8, H_2, etc.) and toxic gases (CO, H_2S, etc.) in indoor as well as outdoor spaces [3–9]. In these sensors, a key role is played by a porous ceramic entity (sensor element) made of an appropriate semiconducting oxide. The ceramic entity, fabricated into a sintered block or a film supported on a substrate, changes its electrical resistance upon exposure to a reducing gas in problem at elevated temperature (e.g., 300°C) so that one can detect or monitor the gas from the magnitude of the change in resistance. Despite such a simple detection principle, the mechanism of gas sensing has been shown to be fairly complex. It is true that the resistance change originates from an interaction between the reducing gas and the metal oxide. It has been pointed out, however, that this interaction takes place through the

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mediation of adsorbed (or surface) oxygen of the metal oxide, not through the adsorption of the reducing gas itself. That is, the reducing gas reacts with the adsorbed oxygen, causing its decrease from an equilibrium concentration level in air. In other words, catalytic oxidation of the reducing gas takes place on the metal oxide, and the resulting decrease of the adsorbed oxygen is eventually monitored as a change in the electrical resistance of the sensor element.

In this way, catalytic properties and semiconducting properties of sensor materials (metal oxides) are combined together to build up the gas sensing function. Thus the gas sensing properties depend naturally on the catalytic or surface chemical properties of sensing materials used, beside their physical or morphological properties such as grain size, porosity and thickness. This has provided a base on which the gas sensing properties have been modified often drastically by the addition of foreign materials (modifiers) to the sensing materials [10]. In fact, many sensors which are sensitive and selective to particular gases have been developed through such modification techniques.

The subject concerned here is the modification of the acid–base properties of sensing materials toward the sensitive detection of ethanol gas (C_2H_5OH) in air. We have reported that the addition of a basic oxide (e.g., La_2O_3) to SnO_2 or In_2O_3 increases the sensitivity to ethanol gas drastically [11,12]. We have pointed out that this phenomenon appears to be related with the reaction routes of ethanol gas which are dependent on the acid–base properties of metal oxide catalysts. However, experimental verification has remained yet to be carried out. In this paper, we tried to elucidate the meaning of the acid–base modification on the SnO_2-based ethanol gas sensor from a view point of catalytic properties.

2. Experimental

The base sensing material used in this study, SnO_2 powder, was a standard sample supplied from the Catalysis Society of Japan. It was synthesized from an aqueous solution of $SnCl_4$ by ammonolysis, followed by calcination at 700°C. The specific surface area of the powder was 20 m^2 g^{-1}. The SnO_2 powder was loaded with various metal oxides by an impregnation method: The powder was suspended in an aqueous solution of the acetate salt of each constituent metal, followed by drying and calcining at 600°C for 5 h. The loading of each metal oxide was fixed to be 5% by weight on the oxide basis.

The sensor element fabricated was of a sintered-block type as schematically shown in Fig. 1. The powder of SnO_2 or foreign oxide-loaded SnO_2 was mixed with water to form a paste, which was applied about 1 mm thick on an
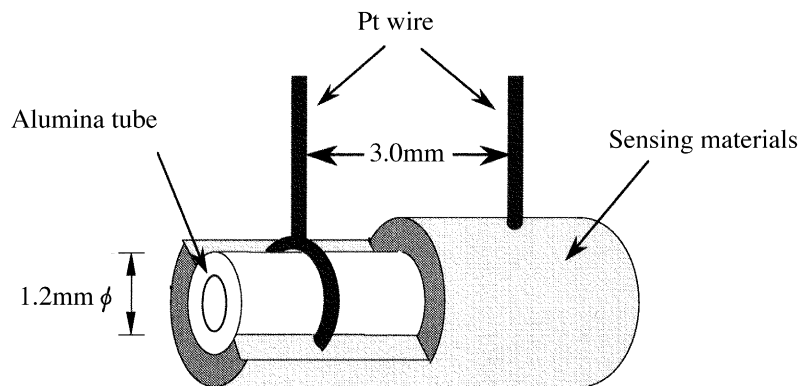

Fig. 1. Structure of sensor element fabricated (partially cut-in view).

alumina tube (1.2 mm in diameter) attached with a pair of Pt electrodes. The green coating was then sintered at 700°C for 4 h in air. Gas sensing experiments were carried out in a conventional gas-flow apparatus. The sensor element set inside a glass chamber was heated to a designate temperature (300°–500°C) externally by an electrical furnace. Synthetic air or ethanol gas (typically 1000 ppm)-containing air was let to flow over the sensor element at a rate of 100 cm^3 min^{-1}, while the electric resistance of the element was measured by using an digital-electrometer (Advantest TR2114). The sensitivity was defined as the ratio of sensor resistance in air (Ra) to that in the ethanol gas containing air (Rg).

Catalytic oxidation experiments were also conducted in a gas-flow apparatus. The same powder samples as used for the sensor elements were pressed, ground and sieved to 28-60 mesh before being packed as a catalyst bed (1.0 g) in a quartz reactor. A gaseous mixture of ethanol gas (1500 ppm) and air was fed to the reactor at a flow rate of 100 cm^3 min^{-1}. The effluents were analyzed by gas chromatography. Catalyst temperature was varied in the range 100°–

600°C. The conversion of ethanol gas was derived from the decrease of ethanol gas concentration due to the reaction, while the conversions to reaction products were derived from the analytical data on the ethanol gas (or total carbon) basis.

3. Results and discussion

3.1. Gas sensing properties

The SnO$_2$-based elements, loaded and unloaded with foreign metal oxides (5 wt.%), were subjected to gas sensing experiments. Fig. 2(a) shows the electrical resistance of each sensor element in air (Ra) as a function of temperature (300°–500°C). The addition of a foreign oxide increased the value of Ra tremendously from that of the pure SnO$_2$ element (around 10^4 Ω): Ra was around 10^8 Ω for the oxide-loaded elements at 300°C except for one loaded with WO$_3$ (around 10^6 Ω). Such an increase in Ra with foreign additives has often been observed for semiconductor gas sensors. The 5 wt.% loading adopted here corresponds roughly to the
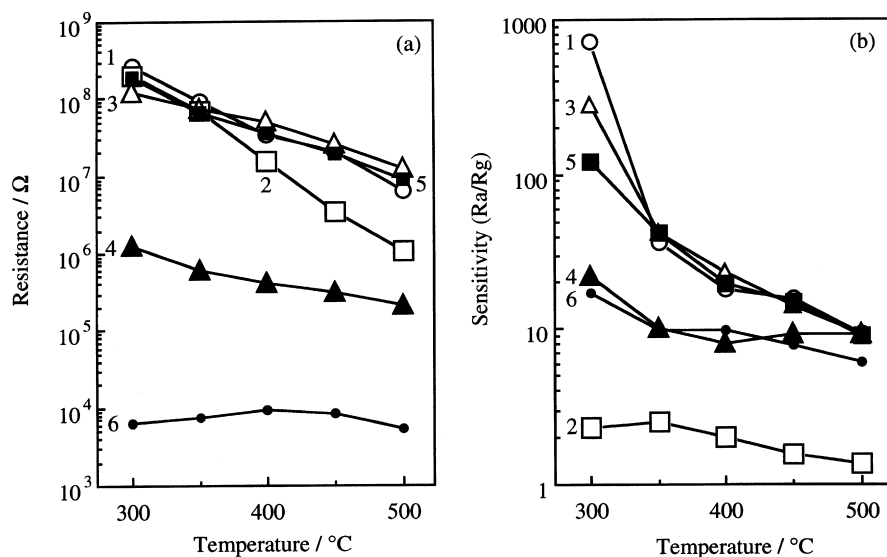

Fig. 2. Electrical resistance (ra) in air (a) and the sensitivity (Ra/Rg) to 1000 ppm C$_2$H$_5$Oh (b) as a function of temperature. 1: La$_2$O$_3$–SnO$_2$, 2: MnO$_2$–SnO$_2$, 3: Sm$_2$O$_3$–SnO$_2$, 4: WO$_3$–SnO$_2$, 5: Cs$_2$O–SnO$_2$, 6: SnO$_2$.

order of one monolayer coverage of SnO_2 surface if the additives are assumed to spread uniformly over the SnO_2 grains. It has been shown that in many cases electronic interactions between the additives and SnO_2 cause such an increase in Ra. However, real causes were left unanswered for the present cases, because the dispersion state of additives was not characterized. Nevertheless, the increase in Ra seems to have no direct relations with the gas sensing properties, as described below.

The electric resistance of each element decreased to a new value (Rg) upon exposure to ethanol gas (1000 ppm). The gas sensitivity ($S = Ra/Rg$) thus obtained is plotted against temperature (300°–500°C) in Fig. 2(b). The S value was the highest at 300°C for each element, tending to decrease with increasing temperature. Obviously the values of S strongly depended on the kinds of additives, especially at 300°C. It may be suspected that S would increase further if temperature is lowered below 300°C. However, this was difficult experimentally, because the rate of response and recovery for most of the sensor elements was degraded

too much to determine the stationary values of Ra and Rg. Even at 300°C, it took about 20 min for the response and recovery transients to reach stationary state.

In order to know what property of the additives is important for the ethanol gas sensitivity, the sensitivity values of all the tested elements are plotted against the electronegativity values of metal cations [13] of the additives (Fig. 3). Based on these data, it is possible to classify the additives into three groups as follows.

- I: Sensitivity promoters consisting of basic metal oxides
- II: Sensitivity inhibitors consisting of oxides of typical d-transition metals (except Ni)
- III: Sensitivity-indifferent additives consisting of acidic metal oxides (WO_3)

Group II additives are known to have rather high catalytic activity for oxidation reactions, and this may be an origin for the inhibiting effects (see below). It is suggestive that all the basic oxides tested belong to group I.
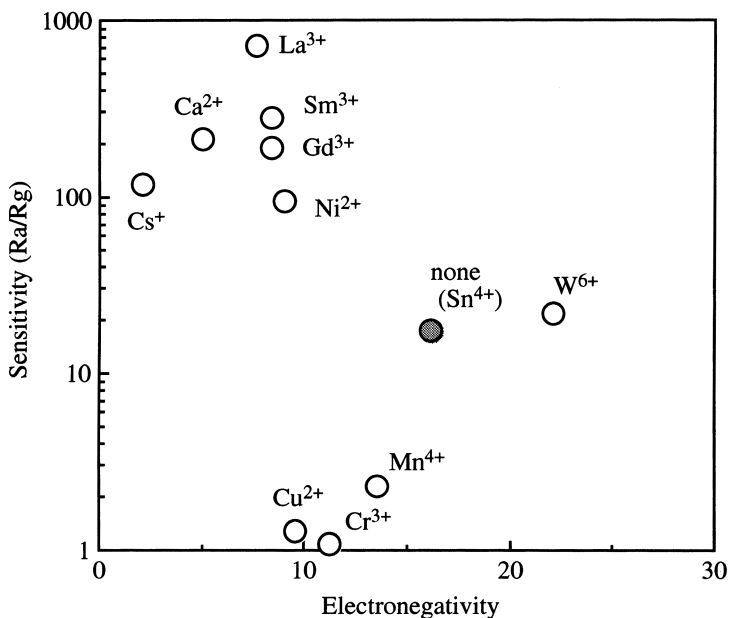

Fig. 3. The sensitivity to ethanol gas as correlated with the electronegativity of metal cations added to SnO_2.

3.2. Catalytic properties

To know the meaning of the acid–base properties of the sensor elements, catalytic properties of the sensing materials was investigated for the reactions of ethanol gas. Five additives, Cs_2O, La_2O_3, Sm_2O_3, MnO_2 and WO_3, were selected to cover a wide electronegativity range of the metal cations. Fig. 4 shows typical examples of the catalytic reactions of ethanol gas (1500 ppm) in air over the four selected catalysts, pure SnO_2 (a), and SnO_2 loaded with La_2O_3 (b), WO_3 (c) and MnO_2 (d). Over the pure SnO_2 catalyst (a), ethanol gas started reaction at 150°C, reaching 90% conversion at 300°C. The primary product from ethanol gas was CH_3CHO, which was converted to CO_2 and CO increasingly at higher temperature. Rather similar reaction behavior of ethanol gas was also observed over La_2O_3–SnO_2 (b), though the temperature range over which the ethanol conversion increased most steeply shifted to the higher temperature side and the conversion to CO_2 became dominant at 300°C. Over WO_3–SnO_2 (c), however, the reaction behavior was quite different: the primary prod-
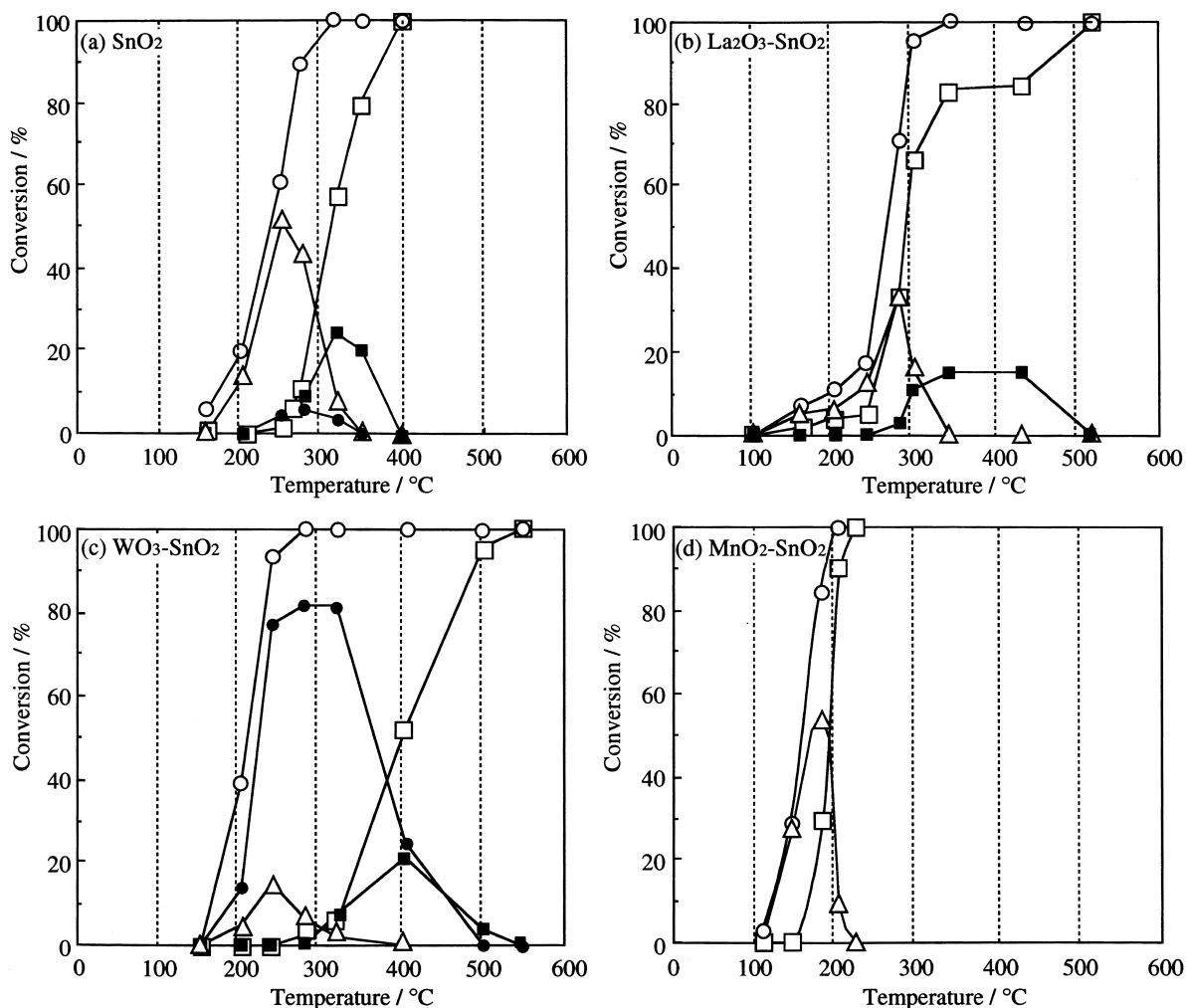

Fig. 4. Temperature dependence of the catalytic reactions of ethanol gas in air over various catalysts. (a) SnO_2, (b) La_2O_3–SnO_2, (c) WO_3–SnO_2, (d) MnO_2–SnO_2. $\bigcirc$, conversion of C_2H_5OH; $\bullet$, conversion to C_2H_4; $\triangle$, conversion to CH_3CHO; $\square$, conversion to CO_2; $\blacksquare$, conversion to CO.

uct was C_2H_4 and the conversion to CO_2 continued to increase rather gradually up to 550°C. Over MnO_2–SnO_2 (d), the reaction started at about 100°C, producing CH_3CHO as a primary product, and 100% conversion was attained already at 250°C.

It has long been known that ethanol gas undergoes two routes of decomposition reactions, i.e., dehydration and dehydrogenation at elevated temperature, depending on the acid–base properties of the oxide catalysts used [14].

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (acidic\ oxide)$$

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \quad (basic\ oxide)$$
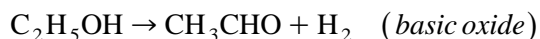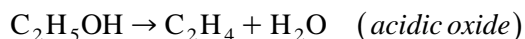
The products thus formed are then oxidized consecutively to CO_2, CO and H_2O. The above schemes coincide well with the observed result that the primary product from ethanol gas changed from CH_3CHO to C_2H_4 as the electronegativity of the metal cation added increased. To discuss this point more quantitatively, relative proportions of the three main products, CH_3CHO, CO_2 and C_2H_4, obtained over each catalyst at the ethanol conversion level of 50% are shown as a function of electronegativity of the added metal cation in Fig. 5. It is seen that C_2H_4 begins to be produced at
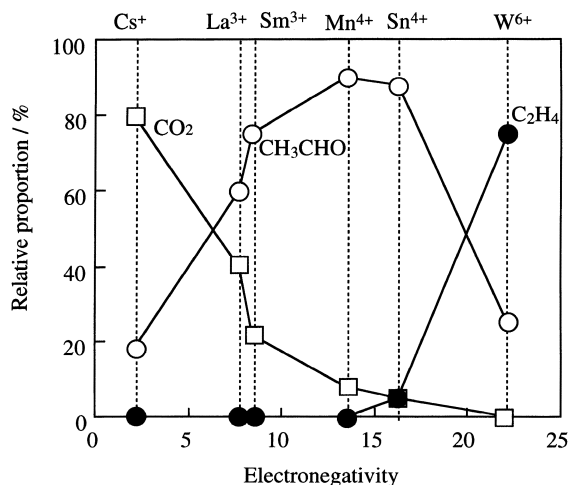

Fig. 6. The temperature for 50% conversion of ethanol gas, $T_{(50\%\ C_2H_5OH)}$, or for 50% conversion to CO_2, $T_{(50\%\ CO_2)}$, as a function of electronegativity of loaded metal cations.

the electronegativity of Sn^{4+}, becoming dominant at W^{6+}, whereas CH_3CHO goes through a maximum at Mn^{4+} and CO_2 decreases monotonically with increasing electronegativity. It is reasonable to consider that CO_2 in these cases is mostly converted from CH_3CHO and that the total of CH_3CHO and CO_2 can be ascribed roughly to the contribution of the dehydrogenation route.

Both the dehydration and dehydrogenation reactions can not affect the electrical resistance of the sensor element unless those are followed by consecutive reactions which consume the adsorbed oxygen. Fig. 6 shows the temperatures at which the conversion of ethanol gas ($T_{(50\%\ C_2H_5OH)}$) and that to CO_2 ($T_{(50\%\ CO_2)}$) reach 50% over each catalyst as a function of electronegativity. These temperatures reflect the catalytic activities for the reactions of ethanol gas and the intermediate products, respectively. It is seen that $T_{(50\%\ CO_2)}$ lowers monotonically as the electronegativity of the added metal cation increases, whereas $T_{(50\%\ C_2H_5OH)}$ goes through a slight minimum at Sm^{3+}. Here the data for MnO_2–SnO_2 are excluded from the discussion, because the data are exceptionally low compared with those of the other catalysts. The catalytic mechanism of MnO_2–SnO_2 may be

Fig. 5. Relative proportions of CH_3CHO, C_2H_4 and CO_2 on the ethanol gas basis as correlated with the electronegativity of loaded metal cations.
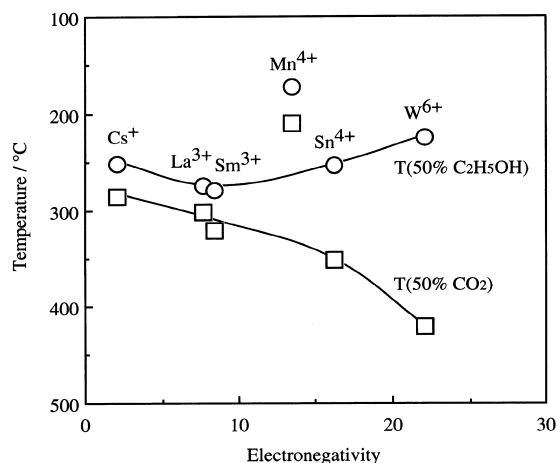
somewhat different from that of the other catalysts. For example, it is possible that MnO_2 acts as a powerful oxidation catalyst by itself, not as a mere modifier of SnO_2. The correlation of $T_{(50\% \ CO_2)}$, if MnO_2-SnO_2 is excluded, indicates that the oxygen-consuming reactions of the intermediates are enhanced as the cation of the additive becomes less electronegative.

3.3. Relation between ethanol gas sensitivity and catalytic properties

The results just mentioned suggest the importance of the rate of oxygen consumption at the operating temperature of sensor elements (300°C) for the discussion of ethanol gas sensitivity. For this purpose, the rate of oxygen consumption over each catalyst was estimated from the previous reaction data at 300°C. The rate was then normalized by the rate of oxygen consumption at which the ethanol gas in the feed (1500 ppm) was completely oxidized. Fig. 7 correlates the ethanol gas sensitivity (S) of each sensor element with the normalized rate of oxygen consumption (r) thus obtained. Roughly

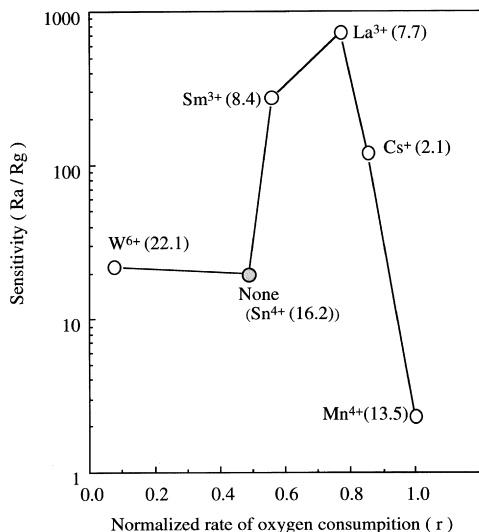Fig. 7. Ethanol gas sensitivity (Ra/Rg) as correlated with normalized rate of oxygen consumption (r) for metal oxide-loaded SnO_2 systems at 300°C. The values in the parenthesis are the electronegativity values.
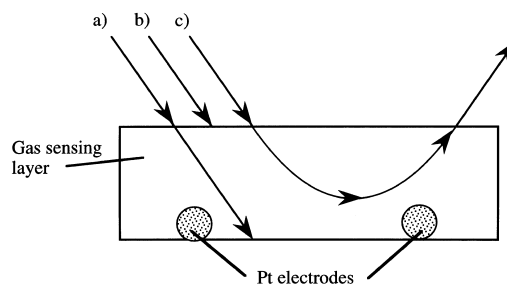

Fig. 8. Influence of catalytic oxidation activity on the depth of gas diffusion inside gas-sensing layer. (a) Appropriate activity ($La_2O_3-SnO_2$); (b) Too high activity (MnO_2-SnO_2); (c) Too low activity (WO_3-SnO_2).

speaking, S goes through a maximum (at La^{3+}) when r increases, while r tended to decrease as the electronegativity of the added cation increased (except for Mn^{4+}). It can be speculated from this correlation that S becomes optimum when r takes an appropriate value, around that of $La_2O_3-SnO_2$, neither too large nor too small. This speculation is consistent qualitatively with what has been observed generally with semiconductor gas sensors.

Fig. 8 shows the relevance of the catalytic oxidation activity with the gas sensitivity schematically. Since the gas sensing layer has a depth from the surface, the gas components to be detected should diffuse in the bulk of sensing layer sufficiently. If the catalytic activity is too large like the case of MnO_2-SnO_2, ethanol gas or its reaction intermediates are consumed out at the surface region of the gas sensing layer, being unable to induce a change in electrical resistance. If the activity is too small like the case of WO_3-SnO_2, on the other hand, the interaction of the sensing layer with the gas becomes too weak to generate strong response. Thus, the sensitivity becomes optimum when the element has an appropriate catalytic activity like $La_2O_3-SnO_2$.

It should be mentioned, however, that the above interpretation in terms of r seems to account only for a part of the reality. It is difficult to explain the big difference in S between SnO_2 and $Sm_2O_3-SnO_2$, the r values of which are comparable. The comparable S val-

ues that SnO_2 and WO_3-SnO_2 exhibit despite the big difference in *r* remain also unexplained. It is suspected that, as an additional factor, one has to consider the rate of recovery of the adsorbed oxygen consumed, or the stationary concentration of unoccupied sites for the oxygen adsorption. It is probable that the adsorption of CO_2 (in the form of CO_3^{2-}) becomes more favored on the basic oxide-loaded SnO_2, giving rise to a hindrance for the readsorption of oxygen. However, this suspicion should be proven experimentally.

4. Conclusions

The ethanol gas sensitivity (*S*) can be increased tremendously with an addition of a basic metal oxide such as La_2O_3 to SnO_2. Ethanol gas undergoes dehydrogenation and dehydration over the SnO_2-based elements loaded with a basic oxide (e.g., La_2O_3) and an acidic oxide (e.g., WO_3), respectively, in agreement with the literature, but such selection of the reaction routes has no direct relations with the behavior of *S*. The consecutive oxidation for the primary products (CH_3CHO and C_2H_4) of ethanol gas is enhanced increasingly as the electronegativity of the metal cation added decreases. This seems to be a reason for the high *S* values of the basic oxide-loaded elements. However, there should be an additional factor which allows the elements to exhibit particularly high *S* values. Promotion of the CO_2-adsorbing properties with the addition of basic oxides can be conceived as such a factor.

Acknowledgements

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