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Bull. Chem. Soc. Jpn., 71, 513—519 (1998)

Molecular-Sieving Gas Sensor Prepared by Chemical Vapor Deposition of Silica on Tin Oxide Using an Organic Template

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(Received May 26, 1997)

A tin(IV) oxide surface was modified by the chemical vapor deposition (CVD) of tetramethoxysilane after the pre-adsorption of benzoate anion as a template to obtain a novel gas sensor with a molecular-sieving function. The sensitivity to large molecules was strongly suppressed by the modification, whereas the sensitivity to small molecules was relatively less modified. It is considered that the silica overlayer with pores whose size was controlled by the template molecule prevented large molecules from reacting with the exposed tin oxide surface, resulting in the molecular-sieving property. The catalytic activity for the oxidation of the alcohol was measured in order to support the idea that the reactivity of organic molecules was suppressed by silica.

Since 1962 when Seiyama et al. found a sensing function on a ZnO-based thin film,[1] semiconductor gas sensors consisting of a metal oxide, such as SnO_2, ZnO or WO_3, has been widely used. The gas sensor is commonly sensitive to various organic and inorganic gases. In other words, the sensor intrinsically has no selectivity to a gas compound. Many attempts have been and are being made to create the necessary selectivity to obtain an intelligent sensor with a molecular-recognition function.[2] These attempts are classified into a modification of the physical structure of the parent oxide[3,4] and an improvement of the chemical reactivity of the surface by the addition of second elements.[5,7]

On a weakly basic metal oxide, such as SnO_2, ZrO_2 or Al_2O_3, we have found that benzaldehyde is adsorbed to form a stable benzoate anion.[8,9] On the other hand, silica is readily deposited to form a monolayer on these weakly basic oxides by the chemical vapor deposition (CVD) of silicon alkoxide.[10—12] Based on these findings, the CVD of tetramethoxysilane (TMOS) was examined on tin oxide after the pre-adsorption of benzaldehyde as a template, in order to obtain a silica overlayer with a porous structure controlled by the template. A molecular-sieving property was generated on tin oxide by this method; molecules larger than the template molecule were hardly adsorbed due to a steric inhibition by the silica overlayer.[13,14] The molecular-sieving property can be adjusted by selecting the size of the template, as observed on a silica overlayer prepared by using α-naphthaldehyde as the template in the place of benzaldehyde.[15] This method is thus promising for precisely designing the molecular-recognition property, and will be available for various oxides.

The sensitivity of a semiconductor gas sensor, namely the change in the electric resistance, is considered to be due to a change in the electron density of the tin oxide by a reaction of the surface oxygen with organic compounds.[16] Because silica is an insulator, the surface of tin oxide covered by silica will be insensitive. When the surface is modified the silica overlayer possessing a molecular-sieving property, it is expected that only small molecules can reach the tin oxide surface to change the electric resistance. Therefore, the CVD method using a template molecule is expected to create selectivity to gas molecules on the gas sensor based on the molecular-sieving function. In the present paper, we discuss the molecular-sieving property for alcohols and aldehydes having various molecular sizes on a tin oxide gas sensor modified by the CVD method. The catalytic activity of the thus-modified oxide was also investigated in order to show how the molecular-sieving property is generated.

Experimental

Preparation of Parent Oxide. SnO_2 was prepared by the hydrolysis of $SnCl_2$. $SnCl_2$ was dissolved in a hydrochloric acid solution. Aqueous ammonia was added to the solution in order to precipitate a gel of $Sn(OH)_2$. The precipitate was washed by water until the pH of solution reached 7, and Cl^- was undetectable. The thus-obtained gel was roughly dried and calcined at 773 K for 2 h. The BET surface area was 22.9 $m^2\,g^{-1}$.

A sample of tin(IV) oxide (1 g) was compressed under a pressure of 29.4 MPa into a disk 10 mm in diameter and 5 mm in thickness, in which two platinum wires were buried. These wires were attached to nickel wires, which were connected to an electric circuit in order to monitor the resistance of the tin oxide disk, as shown in Fig. 1. The thus-molded disk was placed in a 18 mm i.d. Pyrex glass-tube reactor.

Measurement of the Gas-Sensing Property. After a pretreatment in oxygen flow (50 $cm^3\,min^{-1}$) at 673 K, dried air (40 $cm^{-3}\,min^{-1}$) was supplied into the glass tube, and the temperature was cooled down to 543 K. The electric resistance became less, and after several tens of minutes a constant resistance (R_a) was ob-

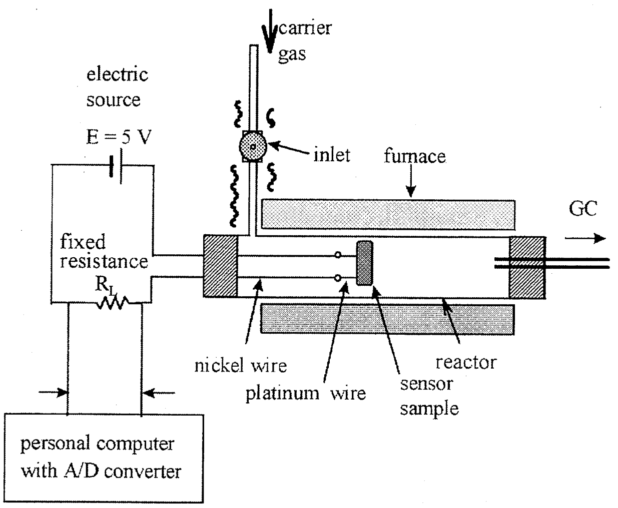

Fig. 1. Experimental apparatus for the measurement of sensitivity and catalytic activity of tin oxide gas sensor.

tained. Then, 0.5 mm^3 of the organic liquid was injected from a microsyringe through a septum installed before the glass tube, and the change in the electric resistance was recorded. Ethanol, isopropyl alcohol, *t*-butyl alcohol, *s*-butyl alcohol, 2-methylcyclohexanol, and benzyl alcohol were used as the alcohols, and propionaldehyde, *n*-butyraldehyde, benzaldehyde, and *o*-tolualdehyde were used as the aldehydes.

The resistance was decreased due to contact with an organic vapor, and was then gradually recovered, as shown in Fig. 2. It took about 1 h to recover the resistance completely. The resistance at the bottom of the negative peak in Fig. 2 was defined as R_g. As shown below, the constant resistance (R_a) was modified by the deposition of silica. Therefore, the sensitivity was shown to be the value normalized by the constant resistance of the sensor sample in air (R_a/R_g).

An FID gas chromatograph with a column of Silicon DC 550 was equipped after the outlet of the reactor to analyze the catalytic activity of the sensor disk. The eluted reactant and the organic products were collected at 159 K for 0.5 h and then fed into the GC.

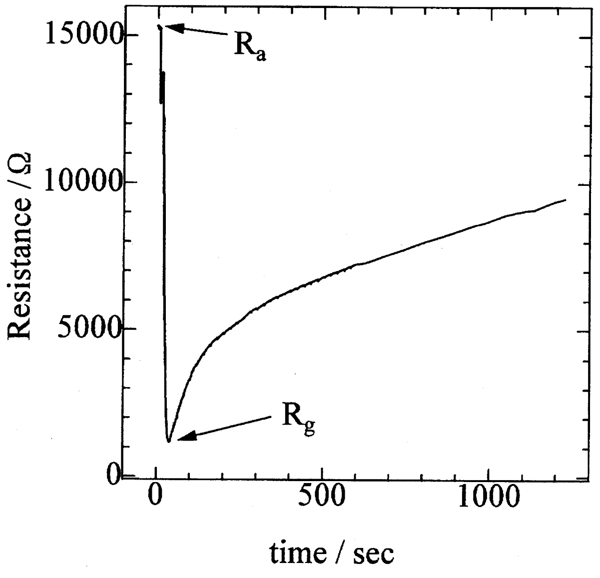

Fig. 2. Change of resistance of unmodified tin oxide by the contact with ethanol.

The conversion of the reactant was calculated with respect to both the organic product and CO_2, based on the assumption that all of the undetectable material was CO_2, as follows:

conversion into organic product = amount of detected product/amount of injected reactant,

conversion into $CO_2 = 1 -$ (sum of amounts of detected products + amount of eluted reactant)/amount of injected reactant.

Preparation of a Silica Overlayer. Tin(IV) oxide was molded into a disk and attached to the electric circuit in the glass tube reactor, as discussed in the previous paragraphs. The disk was pretreated with an O_2 flow (50 cm^3 min^{-1}) at 673 K for 1 h. After the sample was cooled down to 423 K, helium was fed at a 50 cm^3 min^{-1} flow rate. Benzaldehyde (0.5 mm^3) was then injected into the reactor, and a reduction of the electric resistance was observed, presumably due to the adsorption of aldehyde. The resistance gradually decreased along with repeating the injection of benzaldehyde; however, with three times injection, the resistance reached a stable value. Our previous study showed that the surface density of the adsorbed benzoate anion mainly depended on the adsorption temperature, and 1.49 molecules of the benzoate anion were adsorbed on 1 nm^2 of the tin oxide surface at this temperature (423 K). This surface density corresponds to about 70% of the coverage, because the benzoate anion completely covers the surface with 2.1 nm^{-2} of the surface density.[13)]

Then, TMOS was deposited by the CVD method. Vapor of TMOS (2.7 Torr: 1 Torr = 133.3 Pa) was fed from a reservoir cooled with an ice bath. Helium flow with the TMOS vapor was introduced into the reactor at 423 K for 1.5 h. The thus-obtained sample was called Control A. Additional silica-deposition was performed after hydrolysis. The Control A disk was exposed to water vapor (4.58 Torr) at 423 K, and again treated with the TMOS vapor. The disk treated with a three times repetition of the deposition of TMOS and hydrolysis was termed Control B. The electric resistance during the preparation of a silica overlayer was almost constant during the deposition of TMOS and hydrolysis.

Gaseous ammonia (50 cm^3 min^{-1}) was then introduced at 673 K for 0.5 h in order to remove any benzoate anion based on the behavior that benzoate anion reacted with ammonia to be disorbed as benzonitrile.[8)] Finally, oxygen (50 cm^3 min^{-1})flow was introduced at 673 K in order to complete the removal of any residual organics.

As a comparison, a sample (Control C) was prepared without the template. The obtained Control B was treated with water vapor at 423 K, and was then exposed to the TMOS vapor once. The thus-obtained sample was named Control C. The deposited amount of silica is summarized as unmodified $SnO_2(0) <$ Control A $<$ Control B $<$ Control C, because the deposited silicon amount increased along with increasing the repetition number of the deposition and hydrolysis, as shown in a previous study.[13)]

Results

Sensitivity of Gas Sensor. The constant resistance in air (R_a) was changed by the deposition of silica. Figure 3 shows that the constant resistance (R_a) decreased as unmodified $SnO_2 \gg$ Control A $>$ Control B $>$ Control C. The resistance in air seems to decrease with the coverage by silica.

Figure 4 shows the sensitivities to alcohol molecules of various samples. The sensitivities to *s*-butyl alcohol and isopropyl alcohol on an unmodified sensor were especially high. It was hard to find any relationships between the sensitivity and the property of the alcohol molecule. Generally, the sensitivity on Control A was lower than that on unmod-

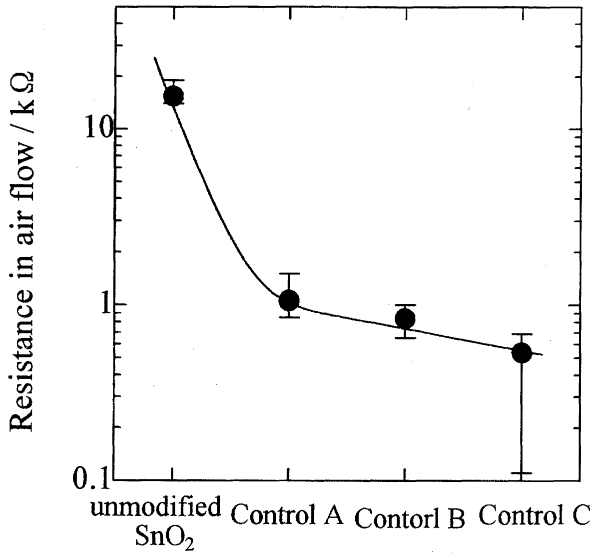

Fig. 3. Change of constrast resistance in air (R_a) by the deposition of silica.

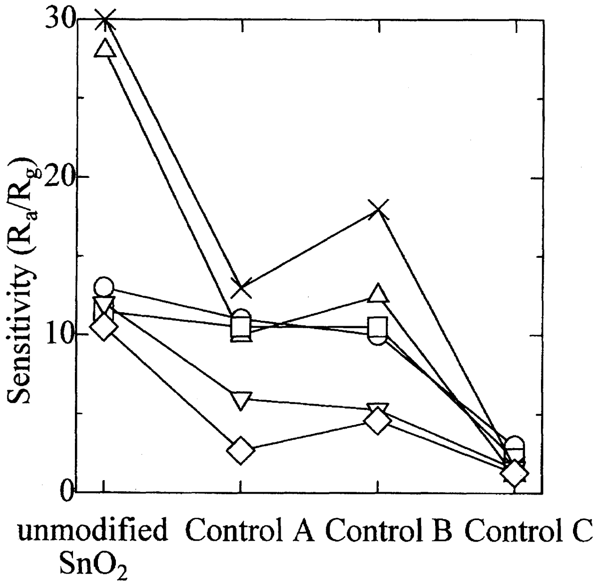

Fig. 4. Sensitivity to ethanol (○), isopropyl alcohol (△), *t*-butyl alcohol (□), *s*-butyl alcohol (×), 2-methylcyclohexanol (▽), and benzyl alcohol (◇) of SnO$_2$ sensor with and without silica overlayer.

ified SnO$_2$, showing that the silica deposition commonly suppressed the sensing function. However, the decrease in the sensitivities to ethanol and *t*-butyl alcohol was relatively small, while the sensitivities to *s*-butyl alcohol, isopropyl alcohol, 2-methylcyclohexanol and benzyl alcohol decreased significantly. This shows that the surface modified by the CVD using the template distinguished the former group of alcohol, i.e., ethanol and *t*-butyl alcohol, from the latter ones, i.e., *s*-butyl alcohol, isopropyl alcohol, 2-methylcyclohexanol, and benzyl alcohol. On Control B, approximately similar sensitivities as those on Control A were observed for all of the alcohols.

Control C showed quite low sensitivities to all of the alcohols. This indicates that the silica layer deposited in the absence of a template, which was presumed to completely cover the surface of Control C, inactivated the sensor surface.

In order to quantify the change in the sensing property by the deposition of silica, the degree of hindrance by the silica overlayer was defined for each organic molecule as

$$H_s = \frac{(R_a/R_g)_s - 1}{(R_a/R_g)_{SnO_2} - 1},$$

where R_a is the resistance in air, R_g is the resistance in an atmosphere containing the organic molecules, and subscript s indicates the sensor sample. When the sensitivity of the silica-deposited sensor is less than that of the unmodified one, the degree of hindrance is larger than 1; in other words, the larger is the degree of hindrance, the lower is the sensitivity relative to that of SnO$_2$. Figures 5 and 6 show the degree of hindrance to alcohol molecules on Control A and Control B, respectively. The sequence of alcohols in the figures is according to the molecular size; from the left to right side of the figure, the molecular size becomes larger, as shown below.

On Control A, H_A for ethanol and *t*-butyl alcohol were close to 1, whereas those for isopropyl alcohol, *s*-butyl alcohol, and 2-methylcyclohexanol were high (2.3—3.0), as shown in Fig. 5. H_A for benzyl alcohol was quite large (5.6). On Control B, H_B for ethanol and *t*-butyl alcohol were slightly higher than 1, and that for *s*-butyl alcohol was about 1.7. The H_B for isopropyl alcohol, 2-methylcyclohexanol, and benzyl alcohol were close to 2.5.

Figure 7 shows the degree of hindrance for the alde-

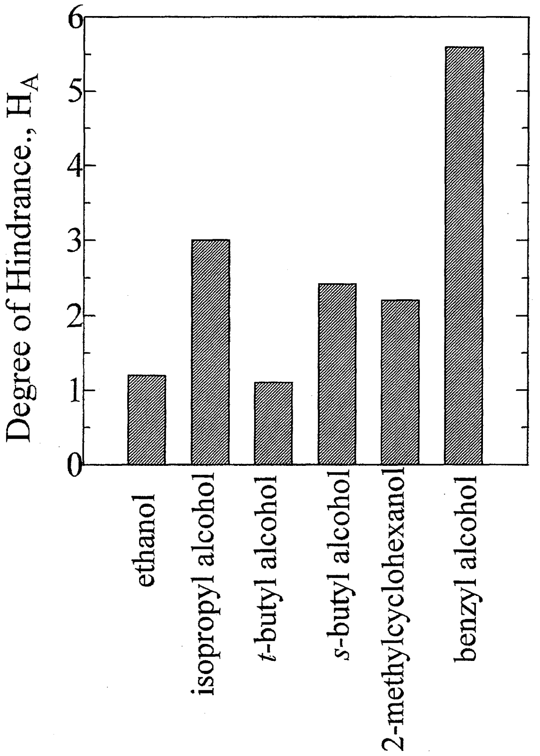

Fig. 5. Degree of hindrance for alcohol molecules on the Control A.

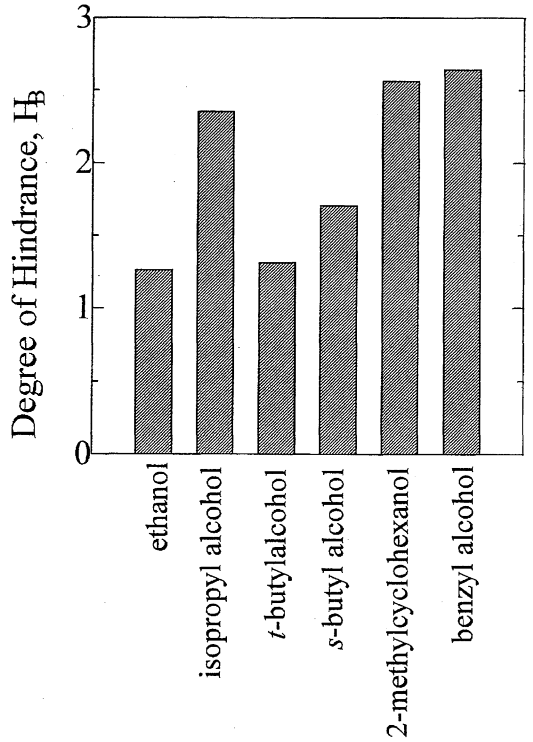

Fig. 6. Degree of hindrance for alcohol molecules on the Control B.

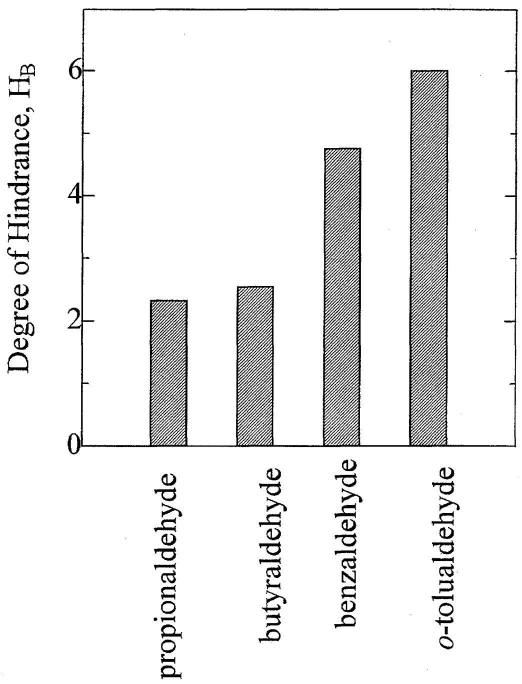

Fig. 7. Degree of hindrance for aldehyde molecules on the Control B.

hyde molecules on Control B. H_B for propionaldehyde and *n*-butyraldehyde were about 2, and those for benzaldehyde and *o*-tolualdehyde were quite large, 4.5 and 6.0, respectively.

Conversion of Alcohols. At the outlet of the reactor, CO_2 and acetaldehyde were observed when ethanol was contacted with the gas sensor. Table 1 shows the conversions of ethanol into CO_2 and acetaldehyde on the samples. The conversion into acetaldehyde was 6% on unmodified SnO_2. Although a small amount of silica enhanced the conversion (Control A), further deposition decreased the conversion (Control B and Control C). On the other hand, the conversion into CO_2 decreased with increasing the amount of deposited silica, as $SnO_2 >$ Control A > Control B > Control C. When *s*-butyl alcohol was injected, CO_2 and methylethylketone were produced. Table 2 shows the conversions from *s*-butyl alcohol into CO_2 and methylethylketone. The conversion into methylethylketone was quite and almost constant on all of the samples (0.1—0.3%). The conversion into CO_2 decreased with the deposition of silica, like that of ethanol.

Discussion

Selectivity of a Silica-Deposited Gas Sensor. As shown above, the silica deposition generally suppressed the sensitivities to the molecules. However, the degree of hindrance by silica deposition using the template, namely, the degrees of hindrance on Control A and B, was different among the organic molecules. Among the alcohols, the degree of hindrance for ethanol and *t*-butyl alcohol was relatively small on Control A and B, while the sensitivities to *s*-butyl alcohol, isopropyl alcohol, 2-methylcyclohexanol, and benzyl alcohol significantly decreased, as shown in Figs. 5 and 6. This shows that a surface modified using the template distinguished the former group of alcohols from the latter ones.

For the aldehyde molecules, the silica overlayer modified using the template (Control B) distinguished propionaldehyde, *n*-butyraldehyde from the benzaldehyde and *o*-tolualdehyde, as shown in Fig. 7. The silica overlayer deposited using the pre-adsorption of template thus distinguished between the two groups of molecules: 1) ethanol, *t*-butyl alcohol, propionaldehyde and *n*-butyraldehyde; 2) *s*-butyl alcohol, isopropyl alcohol, 2-methylcyclohexanol, benzyl alco-

Table 1. Conversion of Ethanol

	Total conversion	Conversion into acetaldehyde	Conversion into CO_2
	%	%	%
Unmodified SnO_2	46	6	40
Control A	53	17	36
Control B	18	12	6
Control C	8	8	0

Table 2. Conversion of *s*-Butyl Alcohol

	Total conversion	Conversion into methylethylketone	Conversion into CO_2
	%	%	%
Unmodified SnO_2	77	0.11	77
Control A	56	0.28	56
Control B	39	0.24	39
Control C	0	0.2	0

hol, benzaldehyde, and *o*-tolualdehyde.

Figure 8 shows the estimated molecular sizes of the used alcohols and aldehydes based on the covalent bond lengths and van der Waals radii of atoms.[17] The molecular size of benzaldehyde, i.e., the template used to prepare the present samples, is estimated to be 0.70 nm. The molecular sizes of ethanol, propionaldehyde, and *n*-butyraldehyde are smaller than that of the template, while isopropyl alcohol, *t*-butyl alcohol, *s*-butyl alcohol, benzyl alcohol, 2-methylcyclohexanol, and *o*-tolualdehyde molecules are similar or larger than benzaldehyde.

Therefore, it is concluded that the silica overlayer de-

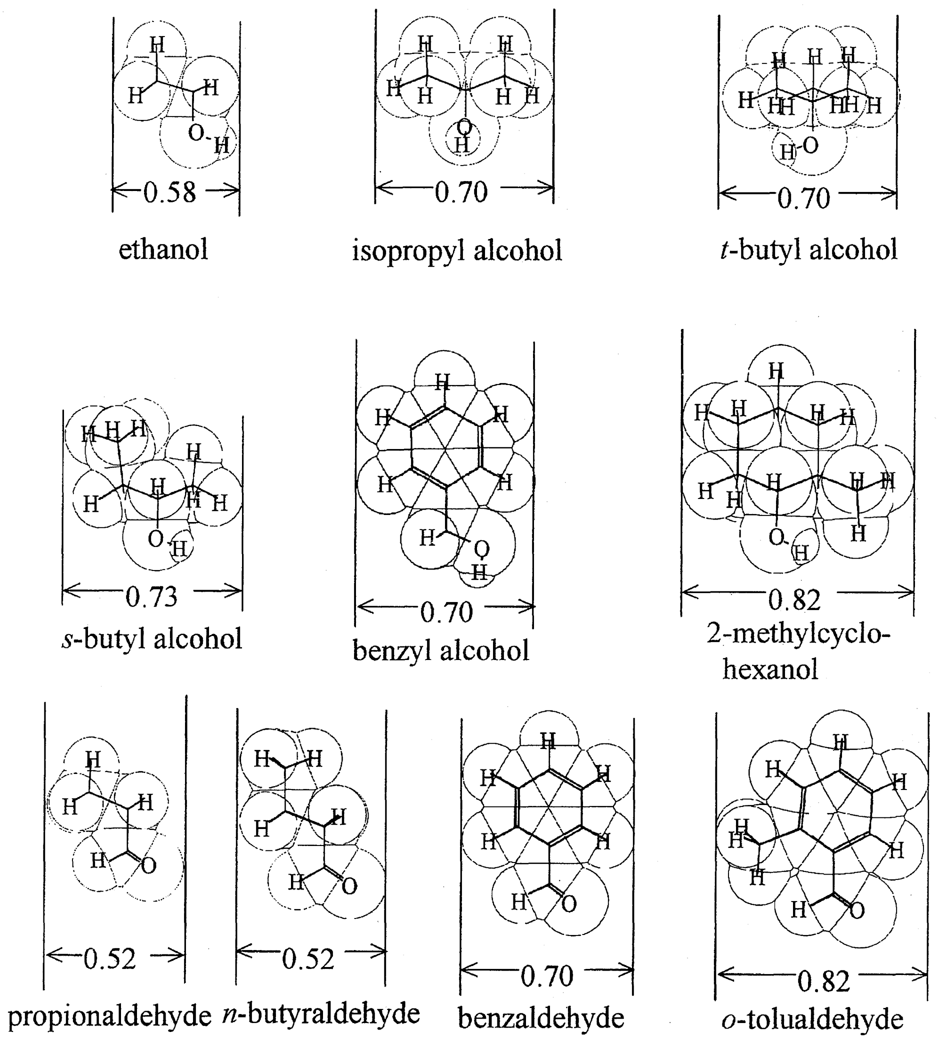

Fig. 8. Estimation of molecular size based on the assumption as follows:
1) The OH group in alcohol is bonded onto the surface.
2) The CHO group in aldehyde is bonded onto the surface.
3) The covalent bond length is 0.11 nm for C–H, 0.14 nm for C–O, 0.12 nm for C=O, 0.15 nm for C–C in single bond, 0.14 nm for C–C in aromatic ring, and 0.94 nm for O–H, respectively.[17]
4) The van der Waals radius of the atom is 0.17 nm for C, 0.15 nm for O, and 0.13 nm for H, respectively.[17]
The estimated molecular size is shown by the arrow in the unit of nm.

posited using the pre-adsorption of the template selectively suppressed the sensitivities to the molecules with similar or larger sizes than 0.7 nm, i.e., the size of the pre-adsorbed template molecule (isopropyl alcohol, *s*-butyl alcohol, benzyl alcohol, 2-methylcyclohexanol, and *o*-tolualdehyde), while the sensitivities to the smaller molecules (ethanol, propionaldehyde, *n*-butyraldehyde) were relatively less affected. However, the experimental results have an exception; like that of ethanol, the sensitivity to *t*-butyl alcohol decreased not so strongly, although *t*-butyl alcohol has a large molecular size (0.70 nm, similar to that of benzaldehyde). It has been found that the silica monolayer created Brønsted acid sites on such basic oxides as Al_2O_3, TiO_2, and ZrO_2.[10,11] The catalytic activity for the dehydration of alcohols on such metal oxides is complicatedly changed by silica deposition; the activity for the dehydration of the *t*-butyl alcohol increased with increasing the amount of deposited silica, whereas the activity decreased for the ethanol.[10,11] It was suggested that the deposited silica on tin oxide, itself, activated *t*-butyl alcohol, presumably via the formation of an intermediate adsorbed on the silica surface. Therefore, it is speculated that the silica enhanced the amount of adsorption of *t*-butyl alcohol in the present case. In such a case, the deposited silica must have no molecular sieving property. Although such an exceptional case was observed, it can be concluded that the silica overlayer deposited using the template generally distinguishes the molecules based on the molecular size.

In contract, Control C, which was prepared by CVD without any pre-adsorption of a template, showed no selectivity for molecules. The molecular recognizing function generated on Control A and B must have been due to the template molecular size.

Sensing Mechanism of Alcohol. The sensitivity to an organic molecule is explained by the consumption of oxygen on a tin oxide surface or by the adsorption of organic molecules on a tin oxide surface.[2]

The conversions of ethanol and *s*-butyl alcohol into CO_2 decreased with increasing the amount of deposited silicon, and reached to 0 on Control C, as shown in Tables 1 and 2. From these results, it is suggested that the surface of Control C was completely covered by a silica overlayer, and presumably had no oxidation activity.

Figures 9 and 10 show the sensitivity for ethanol and *s*-butyl alcohol, respectively, as a function of conversion into CO_2. The sensitivity increased with increasing the conversion into CO_2, indicating that the sensing behavior for alcohol was accompanied by the complete oxidation of alcohol molecules. It is thus confirmed that the silica overlayer hindered the organic molecules from accessing the exposed tin oxide surface which possessed the oxidation activity, which created the molecular-sieving property on the gas sensor.

It is considered that the silica overlayer with pores, whose size was controlled by the template molecule, prevented molecules with similar or larger sizes than the template from reacting with the tin oxide surface, resulting in the molecular-sieving property.

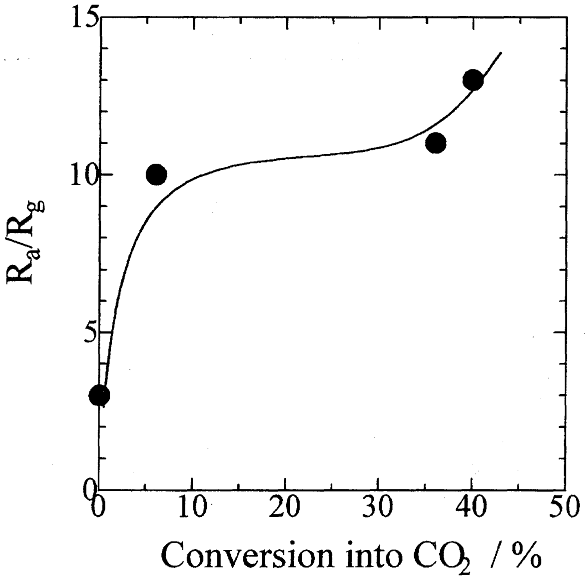

Fig. 9. Relationship between the conversion of ethanol into CO_2 and sensitivity.

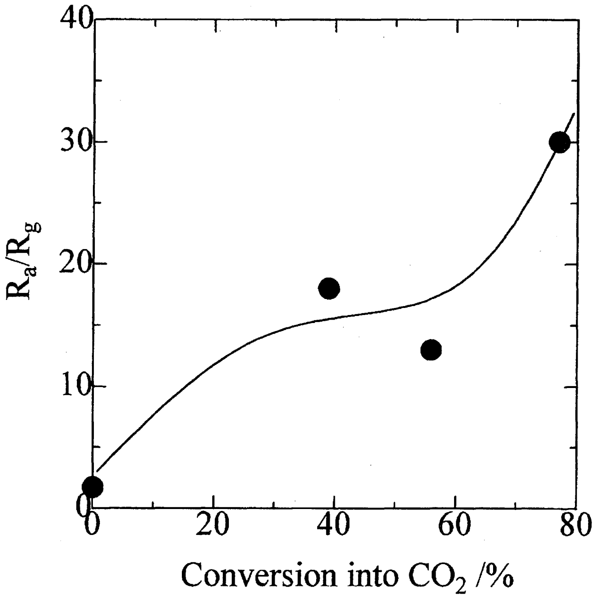

Fig. 10. Relationship between the conversion of *s*-butyl alcohol into CO_2 and sensitivity.

This work was supported by a Grant-in-Air for Scientific Research on Priority Areas of "Electrochemistry of Ordered Interfaces" No. 09237246 from the Ministry of Education, Science, Sports and Culture.

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