— Article —

Detection of Aliphatic Carboxylic Acids Using Tin Oxide Based Gas Sensors

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SnO₂ based gas sensors have been investigated for the detection of aliphatic carboxylic acids (C₂~C₈). Among SnO₂ sensors modified with foreign metal oxide, MoO₃, and WO₃-SnO₂ sensors showed high sensitivities to aliphatic carboxylic acids, although both sensors exhibited different properties from each other. Catalytic properties of SnO₂ based sensor materials have been also evaluated in the oxidation of carboxylic acid in order to be associated with sensing properties. Compared with pure SnO₂, the catalytic activity was decreased and the partial oxidation was favored for WO₃-SnO₂. For MoO₃-SnO₂, the partial oxidation was promoted with the similar activity to pure SnO₂, and the cyclic compound like maleic anhydride was produced in the oxidation of carboxylic acid with carbon number larger than 5. These results mean that the consumption of adsorbed oxygen on the surface of sensor material is decreased due to the addition of WO₃ and MoO₃. It was found that the catalytic activity was too high and most of carboxylic acid were oxidized at sensor surface for pure SnO₂ sensor. On the other hand, for WO₃- and MoO₃-SnO₂ sensors, the catalytic activity was decreased and the partial oxidation was preferred. This causes the consumption of adsorbed oxygen inside the sensor, inducing the enhancement of sensitivity.

Key Words : SnO₂ Gas Sensor, Carboxylic Acid, Catalytic Oxidation, Surface Modification

1 Introduction

These days, there are increasing interests in a detection or discernment of odorous compounds in relation to the application to food, cosmetics, and medical industries as well as amenity or aromatherapy. For this purpose, semiconductor gas sensors such as SnO₂ sensors, which can detect combustible gas from their resistance change, seem to be one of the most suitable sensors because of their high sensitivity and stability. Fukui demonstrated the performance of CaO-SnO₂ sensor in his study on the detection of various odorous compounds, and summarized the sensing properties in relation to the functional group of organic compounds.¹⁾ Recently, 'electronic nose' using a sensor array consisting of plural gas sensors has been actively investigated.²⁾ However, the signal processing was mainly studied in the electronic nose. It seems that the performance of electronic nose increases when the sensor designed for each kind of odor is employed for a sensor array. In semiconductor gas sensors, the surface modification can improve the sensing properties of semiconductor gas sensors.³⁻⁵⁾ Namely, the modification by addition of foreign oxide or precious metal makes sensors possible to have high sensitivity as well as high selectivity to particular gas. Previously, SnO₂ based sensors were investigated for the detection of various odorous compounds such as alcohols,⁶⁾ ketones,⁷⁾ esters,⁸⁾ and terpenes.⁹⁾ The suitable foreign oxide was found for the detection of each odorous compound in these studies.

In the present paper, we focused aliphatic carboxylic

acids (C₂-C₈) as objective gases for a series of odor sensor investigation. The sensing properties of SnO₂-based sensors modified with foreign oxide were systematically examined to detect vapor of aliphatic carboxylic acids. Further, the catalytic properties of SnO₂-based sensor materials were evaluated because the oxidation of organic molecules was deeply associated with sensing property. It is known that acetic acid (CH₃COOH) and propionic acid (C₂H₅COOH) have sharp smell, butyric acid (C₃H₇COOH), valeric acid (C₄H₉COOH), and hexanoic acid (C₅H₁₁COOH) have offensive smell like excrement, and octanoic acid (C₇H₁₅COOH) has butter-like smell. It is considered that the carboxylic acid sensor in the present paper is useful for bad-smelling gas detection, food-processing, and so on.

2 Experimental

The powder of SnO₂ was prepared from SnCl₄ in wet process. The precipitate (stannic acid) obtained by the neutralization of aqueous SnCl₄ solution with aqueous NH₃ was calcined at 650°C for 4 h in air. In order to modify SnO₂ with foreign oxide, the SnO₂ powder was impregnated with metal salt (typically acetate) and calcined at 650°C for 4 h in air. 17 kinds of metal oxides were used here and the loading of them was fixed at 5 wt%. The conventional sintered block-type sensor element, as shown in Fig. 1, was fabricated by using pure and modified SnO₂ powder, and sintered at 700°C for 4 h in air. The crystal structure of modified SnO₂ powder was examined by means of XRD (Rigaku, RINT2200,

Fig. 1 Schematic drawing of sensor element.

CuK α radiation). However, any diffraction peaks assigned to foreign oxide were not observed because of small loading. Thus, the state of metal oxide was presumed from calcination temperature as shown in Fig. 2.

For the measurement of sensing properties, the sensor element was set into the flow apparatus. The electrical resistance of sensor element was measured in wet air and in odor containing wet air at 300–500°C. The sensitivity ($S = R_a/R_g$) was defined as the ratio of resistance in air (R_a) to that in odor (R_g). The wet air was prepared as follows. The dry air was bubbled in deionized water at room temperature to obtain wet air with 100% relative humidity (RH). The wet air (RH=100%) with 20 cm³/min of flow rate was mixed with dry air (80 cm³/min) to obtain wet air (RH=20%) with 100 cm³/min. On the other hand, the odor containing air was prepared by using the diffusion tube.¹⁰⁾ The diffusion tube containing carboxylic acid was set into thermostat (Gastec PD-10), and the constant amount of carboxylic acid vapor was obtained by flowing dry air into thermostat where the diffusion tube was set. The concentration of carboxylic acid was adjusted to 10 ppm by controlling the flow rate of dry air and thermostat temperature, and by choosing size of diffusion tube. Then the carboxylic acid containing air was mixed with wet air to attain wet condition (RH=20%). The wet condition (RH=20%) was chosen as normal humidity level in the atmosphere because odor sensors in this paper are supposed to be generally used in the atmosphere.

The oxidation of aliphatic carboxylic acids on SnO₂-based sensor materials was carried out by using a fixed-bed flow reactor at 150–500°C. The odor containing air (RH=20%) was flown into the reactor in which 1 g of SnO₂ based powder was set. The effluent was analyzed by gas chromatograph-mass spectrometer (Shimadzu GCMS QP-5050A).

3 Results and Discussion

3.1 Sensing properties to aliphatic carboxylic acids

Figure 2 shows the sensitivities to 10 ppm acetic acid of pure SnO₂ and 17 kinds of modified SnO₂ sensors at 300–500°C. For all sensors except for WO₃-SnO₂ sensor, the sensitivity decreased with increasing operating temperature from 300 to 500°C. The modification with metal oxide changed the sensitivity of SnO₂ sensor in different way. The addition of oxides of Sr, Ba, Nd, and Zn enhanced the sensitivity of SnO₂ sensor at 300°C, while the Rb₂O-, ZnO-, and MoO₃-SnO₂ sensors showed the higher sensitivity than pure SnO₂ sensor at

400°C. However, the addition of MnO₂, Co₃O₄, and CuO almost lost the sensitivity to acetic acid of SnO₂ sensor at all temperatures examined. The results of hexanoic acid (C₅H₁₁COOH) detection are shown in Fig. 3. The behavior was similar to that for acetic acid, however, the sensitivity of WO₃-SnO₂ sensor decreased with increasing operating temperature. The behavior for other carboxylic acids was very similar to that to hexanoic acid. The typical response transients are shown in Fig. 4 for MoO₃-SnO₂ sensor to 10 ppm acetic acid. At 300°C, the output voltage sluggishly increased upon exposure to acetic acid and reached steady state after 15 min. On the other hand,

Fig. 2 Sensitivities to 10 ppm acetic acid of SnO₂ based sensors modified with various additives at 300–500°C.

Fig. 3 Sensitivities to 10 ppm hexanoic acid of SnO₂ based sensors modified with various additives at 300–500°C.

Fig. 4 Response transients of $\text{MoO}_3\text{-SnO}_2$ sensor to 10 ppm acetic acid at (a) 300°C, (b) 400°C, and (c) 500°C.

the rates of response and recovery were increased at 400°C. The resistance decreased to steady state within 3 min upon exposure to acetic acid, and recovered to initial level within 15 min when air flow was resumed. At 500°C, the response-recovery characteristics were further improved. However, the sensitivity decreased with increasing operating temperature. Thus, the optimal operating temperature was 400°C from the trade-off of sensitivity and response-recovery characteristics. At optimal temperature of 400°C, it was found that ZnO , MoO_3 , and WO_3 were effective in enhancing the sensitivity of SnO_2 sensor to carboxylic acids.

The sensitivities to carboxylic acids of SnO_2 based sensors were correlated with carbon number of carboxylic acid at 400°C. As a result, two types of correlations were obtained. In one type, the sensitivities almost monotonously decreased with increasing carbon number. Pure,

Fig. 5 Sensitivities to various carboxylic acids of SnO_2 based sensors as a function of carbon number in carboxylic acid.

—○— : Pure SnO_2 , —▲— : ZnO-SnO_2 , —◆— : $\text{MoO}_3\text{-SnO}_2$, —×— : $\text{In}_2\text{O}_3\text{-SnO}_2$.

Fig. 6 Sensitivities to various carboxylic acid of SnO_2 based sensors as a function of carbon number in carboxylic acid. —□— : BaO-SnO_2 , —▲— : NiO-SnO_2 , —●— : $\text{WO}_3\text{-SnO}_2$.

ZnO -, MoO_3 -, and $\text{In}_2\text{O}_3\text{-SnO}_2$ sensors belonged this type among the sensors showed good sensitivity. As shown in Fig. 5, MoO_3 - and ZnO-SnO_2 sensors showed high sensitivities to all of carboxylic acids, especially to $\text{C}_2\text{-C}_4$ acids, suggesting these sensors to be good carboxylic acid sensor. In another type, the sensitivity had a maximum at butyric acid in the sensitivity-carbon number correlation. The WO_3 -, BaO -, NiO-SnO_2 sensors were included in this type as shown in Fig. 6. The $\text{WO}_3\text{-SnO}_2$ sensor exhibited the highest sensitivity ($S=12.9$) to butyric acid, suggesting the $\text{WO}_3\text{-SnO}_2$ sensor to be butyric acid selective sensor.

3. 2 Catalytic oxidation of aliphatic carboxylic acid on SnO_2 based catalysts

A semiconductor gas sensor can detect combustible gas from a resistance change due to consumption of adsorbed oxygen in the oxidation of gas on the surface of sensor material. It is considered that most of additives influences the catalytic properties of SnO_2 in the oxidation of combustible gas and thus changes the sensitivity. In order to elucidate why particular additive was effective in the detection of carboxylic acid using SnO_2 sensor, the catalytic oxidation of carboxylic acids was examined for SnO_2 based catalysts. The catalytic properties were investigated for SnO_2 powders modified with WO_3 and MoO_3 which showed the highest sensitivity in each type of sensitivity-carbon number correlation. The catalytic properties of pure SnO_2 was also examined for comparison.

Figure 7 shows conversions in the oxidation of carboxylic acid on pure SnO_2 catalyst as typical example. The conversion began to increase at 150-250°C and reached almost 100% at 300-350°C. The temperature at which the conversion began to increase depended on kind of carboxylic acid. This temperature was the lowest for butyric acid oxidation, and was the highest for acetic acid oxidation. The catalytic activity was evaluated by using $T_{50\%}$ parameter. $T_{50\%}$ was defined as a temperature at which the conversion reached 50%. The increase in $T_{50\%}$ value means the decrease in catalytic activity. Figure 8 depicted $T_{50\%}$ values in the oxidation of carboxylic acid on

Fig. 7 Conversions of carboxylic acid in the catalytic oxidation on pure SnO_2 as a function of reaction temperature. —○— : Acetic acid, —□— : Propionic acid, —◆— : Butyric acid, —▲— : Valeric acid, —■— : Hexanoic acid, —▼— : Octanoic acid.

Fig. 8 Catalytic activities of SnO_2 based catalysts in the oxidation of carboxylic acid as a function of carbon number. —○— : Pure SnO_2 , —▼— : $\text{WO}_3\text{-SnO}_2$, —◆— : $\text{MoO}_3\text{-SnO}_2$.

pure, WO_3 , and $\text{MoO}_3\text{-SnO}_2$ catalysts as a function of carbon number of carboxylic acid. For pure SnO_2 catalyst, $T_{50\%}$ value was 300°C for acetic acid (C_2) and became minimum for butyric acid (C_4). $T_{50\%}$ changed in the range of $200\text{--}300^\circ\text{C}$. For $\text{WO}_3\text{-SnO}_2$ catalyst, $T_{50\%}$ shifted to higher temperature side compared with those for pure SnO_2 , although $T_{50\%}$ also had minimum for butyric acid. Namely, $T_{50\%}$ changed in the range of $280\text{--}370^\circ\text{C}$ for $\text{WO}_3\text{-SnO}_2$. Further, $T_{50\%}$ was 370°C in the oxidation of acetic acid, suggesting the low catalytic activity of $\text{WO}_3\text{-SnO}_2$. It is considered that acetic acid is hardly oxidized on $\text{WO}_3\text{-SnO}_2$ at 300°C , inducing the low sensitivity at this temperature as shown in Fig. 2. On the other hand, $T_{50\%}$ for $\text{MoO}_3\text{-SnO}_2$ varied in the similar range to pure SnO_2 . These results suggest that butyric acid is easily oxidized irrespective of catalyst and that the addition of WO_3 decreased the catalytic activity and $\text{MoO}_3\text{-SnO}_2$ had similar activity to pure SnO_2 .

In order to elucidate the reaction pass, the intermediates produced at low temperature before completely oxidized to CO_2 and H_2O were investigated in detail. The intermediates produced in the oxidation of carboxylic acid on SnO_2 based catalysts are summarized in Table 1. Depending on the intermediates produced, the reactants were classified into 3 groups. In the oxidation of acetic acid (C_2), which belonged the first group, only formaldehyde (C_1) was formed on all catalysts. However, the intermediates were more complicated with increasing carbon number of carboxylic acid. In group II which includes C_3 and C_4 carboxylic acids, aldehydes and alkenes were produced in the oxidation of carboxylic acid. On the other hand, from the group III ($\text{C}_5\text{--}\text{C}_8$ carboxylic acids), the cyclic compounds like furan and maleic anhydride were observed in addition to aldehydes and alkenes. Further, in the oxidation of groups II and III carboxylic acids, alkenes were not observed on pure SnO_2 catalyst, and acetic acid was conspicuously observed on

Table 1 Intermediates produced in the oxidation of carboxylic acid on SnO_2 based catalysts.

Group	Reactant	Catalyst		
		Pure SnO_2	$\text{WO}_3\text{-SnO}_2$	$\text{MoO}_3\text{-SnO}_2$
I	CH_3COOH (C_2)	HCHO (C_1)	HCHO (C_1)	HCHO (C_1)
II	$\text{C}_2\text{H}_5\text{COOH}$ (C_3)	$\text{C}_1\text{--}\text{C}_2$ aldehydes	$\text{CH}_2=\text{CH}_2$ (C_2) $\text{C}_1\text{--}\text{C}_2$ aldehydes	$\text{CH}_2=\text{CH}_2$ (C_2) CH_3COOH $\text{C}_1\text{--}\text{C}_2$ aldehydes
	$\text{C}_3\text{H}_7\text{COOH}$ (C_4)	$\text{C}_1\text{--}\text{C}_3$ aldehydes	C_2 , C_3 alkenes $\text{C}_1\text{--}\text{C}_3$ aldehydes	C_2 , C_3 alkenes CH_3COOH C_2 aldehydes
III	$\text{C}_4\text{H}_9\text{COOH}$ (C_5)	$\text{C}_1\text{--}\text{C}_4$ aldehydes Furan	C_3 , C_4 alkenes $\text{C}_1\text{--}\text{C}_4$ aldehydes Furan Maleic anhydride	CH_3COOH $\text{C}_1\text{--}\text{C}_4$ aldehydes C_3 , C_4 alkenes Furan Maleic anhydride
	$\text{C}_5\text{H}_{11}\text{COOH}$ (C_6)	$\text{C}_1\text{--}\text{C}_5$ aldehydes Furan	C_4 , C_5 alkenes $\text{C}_1\text{--}\text{C}_5$ aldehydes Maleic anhydride	CH_3COOH C_4 , C_5 alkenes $\text{C}_1\text{--}\text{C}_5$ aldehydes Maleic anhydride
	$\text{C}_7\text{H}_{15}\text{COOH}$ (C_8)	$\text{C}_1\text{--}\text{C}_7$ aldehydes Maleic anhydride	C_7 alkene $\text{C}_1\text{--}\text{C}_7$ aldehydes Maleic anhydride CH_3COOH	CH_3COOH $\text{C}_1\text{--}\text{C}_7$ aldehydes C_7 alkene Maleic anhydride

MoO₃-SnO₂ catalyst. From the results of intermediates, the simple rule was easily found for all of reactants and SnO₂ based catalysts as follows. In the oxidation of carboxylic acid with carbon number of n (C _{n} carboxylic acid), C₁~C _{$n-1$} aldehydes, C _{$n-2$} and C _{$n-1$} alkenes ($n \geq 2$), and C₄ cyclic compounds such as furan and maleic anhydride ($n \geq 5$) were formed as intermediates.

The results in the oxidation of propionic acid (C₃) on SnO₂ based catalysts are shown in Fig. 9 as typical example of group II carboxylic acid. The normal axis means the amount of gas included in 1 cm³ of effluent. On pure SnO₂ catalyst, acetaldehyde was produced at 200-350°C

Fig. 9 Amount of product in the oxidation of propionic acid on SnO₂ based catalysts as a function of reaction temperature. (a) Pure SnO₂, (b) WO₃-SnO₂, (c) MoO₃-SnO₂. —○— : Acetaldehyde, —▼— : Ethylene, --□-- : Formaldehyde, ---■--- : Acetic acid.

as major product, while ethylene and acetaldehyde were dominantly produced on WO₃, and MoO₃-SnO₂ catalysts. But, these appeared at higher temperature on WO₃-SnO₂ catalyst. Further, acetic acid was largely detected on MoO₃-SnO₂ catalyst. As an example of group III carboxylic acid, the results in the oxidation of valeric acid are shown in Figs. 10-12 for pure, WO₃, and MoO₃-SnO₂ catalysts, respectively. On pure SnO₂, butyraldehyde was major product, and C₁~C₃ aldehydes and furan (C₄) were also observed at 200-350°C. On WO₃-SnO₂ catalyst, propene (C₃) and 1-butene (C₄), and propionaldehyde (C₃) and butyraldehyde (C₄) were dominantly produced at 250-400°C, while formaldehyde (C₁) and acetaldehyde (C₂) were observed at higher temperature. On the other hand, on MoO₃-SnO₂ catalyst, formaldehyde (C₁) and acetaldehyde (C₂) were produced at 200-400°C after small formation of propionaldehyde (C₃) and butyraldehyde (C₄), while 1-butene (C₄) and propene (C₃), maleic anhydride (C₄), and acetic acid (C₂) were also observed as major products. From the behavior of aldehydes formation, C₁, C₂ aldehydes are considered to be consecutive products from C₃, C₄ aldehydes. Further, it is noteworthy on MoO₃-SnO₂ that maleic anhydride still remains at elevated temperature higher than 400°C and that acetic acid is largely produced. From the temperature at which intermediates were formed, it was found that the catalytic activity increased in the order of WO₃-SnO₂ < MoO₃-SnO₂ ≈ pure SnO₂. This was in good agreement with the result of Fig. 8. Moreover, at optimal operating temperature of 400°C for SnO₂ based sensors, any intermediates were not observed on pure SnO₂, while some of intermediates remained for WO₃ and MoO₃-SnO₂. This suggests that the complete oxidation of carboxylic acid proceeds on pure SnO₂, while the partial oxidation is preferred on WO₃ and MoO₃-SnO₂. The feature of catalytic properties is summarized as follows.

1) Pure SnO₂ has high catalytic activity in the oxidation of carboxylic acid. The complete oxidation proceeds on pure SnO₂ at 400°C.

Fig. 10 Amount of product in the oxidation of valeric acid on pure SnO₂ catalyst as a function of reaction temperature. —○— : Butyraldehyde, --□-- : Propionaldehyde, ---■--- : Furan, --▲-- : Acetaldehyde, ---●--- : Formaldehyde.

Fig. 11 Amount of product in the oxidation of valeric acid on $\text{WO}_3\text{-SnO}_2$ catalyst as a function of reaction temperature.

(a) Aldehydes, (b) Alkenes and cyclic compounds.

—○— : Butyraldehyde, --□-- : Propionaldehyde,
 --▲-- : Acetaldehyde, --▴-- : Formaldehyde,
 —▾— : 1-Butene, ---□--- : Propene, --■-- : Furan,
 —●— : Maleic anhydride.

Fig. 12 Amount of product in the oxidation of valeric acid on $\text{MoO}_3\text{-SnO}_2$ catalyst as a function of reaction temperature.

(a) Aldehydes, (b) Alkenes, cyclic compounds, and others.

—○— : Butyraldehyde, --□-- : Propionaldehyde,
 --▲-- : Acetaldehyde, --▴-- : Formaldehyde,
 —▾— : 1-Butene, ---□--- : Propene --■-- : Furan,
 —●— : Maleic anhydride, --+-- : Acetic acid.

2) $\text{WO}_3\text{-SnO}_2$ not only has lower catalytic activity than pure SnO_2 , but also favors the partial oxidation at 400 $^{\circ}\text{C}$.

3) $\text{MoO}_3\text{-SnO}_2$ has similar catalytic activity to pure SnO_2 , but the partial oxidation is preferred at 400 $^{\circ}\text{C}$.

The possible reaction pass in the oxidation of C_n carboxylic acid was considered as shown in Fig. 13. It is known that hydroxyl group is added to α or β position of carboxyl acid when the acid is oxidized in wet air, and these additions are called as α - or β -hydroxylation. When hydroxyl group is added to α -position, CO_2 is removed from the molecule to form alcohol like intermediate with carbon number of (n-1). On the other hand, CH_3COOH is removed from the β -hydroxylized molecule to form alcohol like intermediate with carbon number of (n-2). Further, alcohol like intermediate is oxidized to produce aldehydes by dehydrogenation or alkenes by dehydration. The surface acid-base property of catalyst determines which reaction of dehydrogenation or dehydration dominantly proceeds in the oxidation of alcohol.¹¹⁾ SnO_2 is known to be slightly basic oxide and thus the dehydrogenation to form aldehydes is favored on pure

Fig. 13 Reaction route in the oxidation of carboxylic acid on SnO_2 based catalyst.

SnO₂. On WO₃- and MoO₃-SnO₂ catalysts, the surface of SnO₂ is modified to acidic because WO₃ and MoO₃ are acidic oxide. The dehydration to alkene is preferred on WO₃- and MoO₃-SnO₂. In the oxidation of acetic acid, only α -hydroxylation occurs to form methanol like intermediate. This is consecutively oxidized only to formaldehyde by dehydrogenation. When the carbon number is larger than 5, it is possible that C₄ alcohol like intermediate is dehydrogenated and cyclized to form furan. Furan is consecutively oxidized to form maleic anhydride. At last, these compounds are completely oxidized to CO₂ and H₂O. It is considered that aldehydes with smaller carbon number are formed due to the oxidation of C_{n-1} or C_{n-2} carboxyl acid intermediate produced from C_{n-1} or C_{n-2} aldehyde intermediate.

3. 3 Relationship between sensing properties and catalytic properties

Xu *et al.* investigated the dispersion of foreign oxide and electronic interaction in SnO₂-based powders.¹²⁾ Among foreign oxides related to the present study, Co₃O₄ tended to aggregate to grow large particle on SnO₂ surface. On the other hand, most of oxides other than Co₃O₄ highly dispersed as fine grains on SnO₂ surface and did not affect the electrical properties of SnO₂ so much. Thus, it is considered that the foreign oxide influences the morphology as well as the surface properties of SnO₂ and that these factors totally affect the catalytic properties. The catalytic properties of SnO₂, WO₃-SnO₂, and MoO₃-SnO₂ were qualitatively correlated with the sensing properties as described below.

It is noted that the inverse curve for WO₃-SnO₂ in Fig. 8 is very similar to sensitivity curve for WO₃-SnO₂ in Fig. 6. This suggests that 280°C of T_{50%} is optimal for high sensitivity and this condition is realized for butyric acid sensing by WO₃-SnO₂ sensor. For other carboxylic acids, the WO₃-SnO₂ sensor showed low sensitivity because of low catalytic activity. On the other hand, pure SnO₂ showed T_{50%} = 295°C for acetic acid and catalytic activity increased with increasing carbon number until C₄. The sensitivity of pure SnO₂ sensor was the highest for acetic acid and decreased with increasing carbon number. Thus, it is seen that the sensitivity is the highest at moderate catalytic activity (T_{50%} = 280°C) and that the lower or the higher activity decreases the sensitivity. The resistance is measured at the part between electrodes inside the sensor element as shown in Fig. 1. The resistance change at this part contributes the sensitivity of sensor. When the catalytic activity is too low, the consumption of adsorbed oxygen is small at this part, inducing low sensitivity. With the moderate activity, the adsorbed oxygen is effectively consumed at this part, resulting in high sensitivity. However, when the activity is too high, the combustible gas is oxidized at surface of sensor element and can not

diffuse inside the element. In this case, the sensitivity is decreased. The pure SnO₂ sensor showed the moderate or low sensitivities to carboxylic acids because of high catalytic activity of pure SnO₂, while the addition of WO₃ decreased the catalytic activity, enhancing the sensitivity. It is considered that the results in the present study are the first example that the high sensitivity is obtained by decreasing well the catalytic activity.

On the other hand, MoO₃-SnO₂ had similar activity to pure SnO₂, but the MoO₃-SnO₂ sensor showed the higher sensitivity than pure SnO₂ sensor. The partial oxidation preferentially occurred on MoO₃-SnO₂, suggesting that the consumption of adsorbed oxygen was smaller than pure SnO₂ on which complete oxidation was favored. For MoO₃-SnO₂ sensor, the products of partial oxidation would diffuse into the part between electrodes and would be oxidized, inducing the enhancement of sensitivity.

Although both WO₃ and MoO₃ made the SnO₂ surface acidic, the catalytic properties were modified in different way because the catalytic activity and intermediates produced were different from each other in WO₃- and MoO₃-SnO₂ as aforementioned. These modifications totally affect the consumption of adsorbed oxygen, inducing the difference in sensing properties. Thus, it is considered that the WO₃-SnO₂ sensor exhibited the optimal oxygen consumption for butyric acid sensing and thus the sensor showed the maximum sensitivity to butyric acid.

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