VOC sensing behavior of semiconducting $\text{Sm}_2\text{O}_3/\text{SmFeO}_3$ mixtures

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$\text{Sm}_2\text{O}_3/\text{SmFeO}_3$ mixed powders were applied to a chemo-resistive VOC (volatile organic compound) gas sensor. The sensor response to 30 ppm toluene gas increased with increasing the Sm_2O_3 content up to 30 wt %, but decreased by further adding. The addition of Sm_2O_3 up to 30 wt % also enhanced the catalytic activity for toluene oxidation, as the result of the sensor response. The amount of toluene adsorption increased with increase in the surface Sm concentration. It was concluded that adding Sm_2O_3 increased the amount of adsorbed VOCs, resulting in the enhancement of the sensor response and the catalytic activity. Furthermore, adding Sm_2O_3 remarkably shortened the recovery time from the VOCs to air. For the ethanol sensing, adding Sm_2O_3 was only effective on shortening the recovery time.

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1. Introduction

SmFeO_3 perovskite-type oxide having p-type semiconducting feature has been investigated as a chemo-resistive sensor material, especially for detecting oxidative gases such as NO_2 and ozone.^{1)–5)} Previously we conducted an XPS analysis on the surface chemical compositions of the series of LnFeO_3 oxides ($\text{Ln} = \text{La}, \text{Sm}, \text{Nd}, \text{Dy}$ etc.).⁵⁾ By this analysis, we found that the surface of SmFeO_3 was specifically rich in Sm, and concomitantly rich in the number of adsorbed oxygen. This result strongly suggests that the surface Sm concentration would correlate with the amount of the adsorbed oxygen. According to such the surface property, among the LnFeO_3 oxides, SmFeO_3 exhibited specifically high sensitivity to the oxidative gases.⁶⁾ High oxidation activity for hydrocarbons has been reported for perovskite oxides containing Sm ion.^{7),8)} Therefore perovskite oxides can be also good candidates for a VOC (volatile organic compound) sensing material. We recently reported on VOC detection using the SmFeO_3 sensor, where the sensor exhibited good responses especially to the aliphatic VOC gases at below 1 ppm.⁹⁾ This good response was explained in terms of a competitive adsorption between the VOC and oxygen molecules, where an adsorption equilibrium constant of VOC molecule is much larger than that of oxygen molecule. In other words, the surface of SmFeO_3 would have a large affinity to the VOC molecules. Previously VOC detection was also conducted with the potentiometric sensor with the cell structure of air, Pt/YSZ/Pt, VOC, air.¹⁰⁾ In that study, covering the Pt electrode on the VOC side with Sm_2O_3 particles significantly enhanced the response to the VOCs and reduced the response time. It was deduced that the Sm_2O_3 layer acted as a VOC condenser. This result may support that the good response of the SmFeO_3 sensor to the VOC molecules is partially due to the Sm-enriched surface where the surface Sm acts as a VOC adsorption site.

In this study, in order to increase the surface Sm concentration of SmFeO_3 , Sm_2O_3 was further added on SmFeO_3 particles and catalytic activity and sensor response to VOC molecule was evaluated.

2. Experimental

2.1 Preparation of $\text{Sm}_2\text{O}_3/\text{SmFeO}_3$ mixed powders

SmFeO_3 powders were prepared by the thermal decomposition of a $\text{Sm}[\text{Fe}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$ heteronuclear complex in air at 600°C for 24 h. The complex was prepared by the same route as that reported in elsewhere.⁶⁾ The prepared SmFeO_3 powder was dispersed in distilled water where prescribed amount of $\text{Sm}(\text{NO}_3)_3$ was dissolved. The suspension was continuously stirred for one day and slowly evaporated in a hot water bath. The resultant mixture was then heated at 600°C for 2 h to obtain a $\text{Sm}_2\text{O}_3/\text{SmFeO}_3$ composite powder. The composite powders were characterized by XRD (X-ray diffraction; Rigaku Co. Rint 2000 Cu-K α). The surface analysis for the composite powders was carried out by XPS (X-ray photoelectron spectroscopy; Perkin-Elmer XPS 1600E, Mg-K α excitation source). Binding energy was calibrated with that of the C-1s peak. The specific surface areas of the powder samples were measured with BET analysis using N_2 adsorbent (BEL Japan, BELSORP Max). Before the measurement, the samples were heat treated at 200°C for 2 h to remove adsorbed water. The amounts of the VOCs adsorption were determined at 25°C by the same manner using the corresponding adsorbents.

2.2 Preparation of sensor elements and their operation

$\text{Sm}_2\text{O}_3/\text{SmFeO}_3$ powders containing 0–50 wt % Sm_2O_3 were added with a small amount of α -terpineol to form a slurry. The slurry was screen-printed on an alumina substrate with Au comb-type electrodes where the electrode gap is 200 μm . After that the film was dried at 100°C and fired at 800°C for 1 h.

A sensor element was mounted on a sample holder and wired with Au-lead using Au-paste and set in a quartz tube in a tubular

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electric furnace. In this study, toluene was used as a test gas. The air-balanced 30 ppm toluene and ethanol gases were regulated with a diffusion tube put in the gas permeator (GASTEC PD-1B). Sensor resistance was monitored by the digital electrometer (Keithley 6514).

2.3 Evaluation of catalytic activities

Catalytic activity of the Sm₂O₃ added SmFeO₃ powders for toluene oxidation was evaluated by the fixed-bed flow reactor. Prescribed amount of the catalyst powders were placed in a Pyrex U-tube between quartz wools. The air-balanced toluene and ethanol gases regulated by the permeator were fed into the glass tube at a space velocity of 40,000 ml/gh. VOC conversion was measured by gas chromatography with a FID detector (Shimadzu GC-8A).

3. Results

3.1 Characterization of the Sm₂O₃/SmFeO₃ mixed powders

Figure 1 shows XRD patterns of the Sm₂O₃/SmFeO₃ powders calcined at 800°C. In addition to the SmFeO₃ phase, the signal due to a cubic Sm₂O₃ phase was observed at 28°. The signal intensity of Sm₂O₃ was monotonously increased with the increase in the Sm₂O₃ content. Any peak shift was not observed for the SmFeO₃ phase, which means no solid solutions between the two phases were formed. We previously found by the XPS measurement that SmFeO₃ rich in the surface Sm are simultaneously rich in adsorbed oxygen.⁶⁾ From this result, it was suggested that Sm

could act as an oxygen adsorption site. In this study, we also conducted XPS analysis for the series of the Sm₂O₃/SmFeO₃ powders. The surface chemical compositions of Sm, adsorbed oxygen and lattice oxygen are shown in **Table 1**. The SmFeO₃ particle prepared in this study also has Sm enriched surface. Surface Sm concentration was monotonously increased with increasing the Sm₂O₃ content. **Figure 2** shows SEM images of the SmFeO₃ and Sm₂O₃/SmFeO₃ powders. All the samples consisted of fine particles ranging from 0.1 to 0.4 µm in their particle sizes. **Figure 3** shows SEM-EDX images of the SmFeO₃ and 30 wt % Sm₂O₃/SmFeO₃ powders. The elemental mappings for both the powders revealed homogeneous distributions of Fe and Sm elements, indicating Sm₂O₃ and SmFeO₃ particles are homogeneously mixed in the powders. The O-1s XPS spectra are shown in **Fig. 4**. Two peaks were observed at 528.5 and 530.6 eV for SmFeO₃. The two peaks at higher and lower binding energies can be attributed to lattice oxygen and adsorbed oxygen, respectively. Li et al.¹¹⁾ also observed two O-1s peaks in the XPS spectra of oxygen species on the surface of ZnO thin films. They assigned the peaks at high (532 eV) and low (530 eV) binding energies to adsorbed oxygen species and O²⁻ in the lattice. Tabata et al.¹²⁾ also obtained two O-1s peaks at around 531.5 and 529.5 eV on LaMn_{1-x}Cu_xO_{3+λ} and made similar assignment for the peaks. The peak intensity of the lattice oxygen is larger than that of the adsorbed oxygen. For Sm₂O₃, lower binding energy was identical to SmFeO₃, but higher binding energy was 531.5 eV, that was even higher than that of SmFeO₃. By contrast to the SmFeO₃ case, the peak intensity of the adsorbed oxygen of Sm₂O₃ is higher than that of the lattice oxygen. By the Sm addition on SmFeO₃, the higher binding energy peak shifted to be close to that of Sm₂O₃,

Fig. 1. XRD patterns of the Sm₂O₃/SmFeO₃ (0–50 wt %) and Sm₂O₃ powders.

Fig. 2. FE-SEM images of the Sm₂O₃/SmFeO₃ powders (0, 10, 30 and 50 wt %).

Table 1. XPS analysis for the surface elemental ratios of Sm, adsorbed oxygen (O_{ad}) and lattice oxygen (O_{lattice})

Sm ₂ O ₃ content (wt %)	Surface elemental ratios				
	Sm Sm + Fe	O _{ad} Sm + Fe	O _{lattice} Sm + Fe	O _{ad} + O _{lattice} Sm + Fe	O _{ad} Sm
0	0.70	0.55	0.88	1.43	0.79
10	0.76	0.53	0.86	1.39	0.70
20	0.84	0.71	0.75	1.46	0.84
30	0.87	0.63	0.73	1.36	0.73
40	0.88	0.82	0.66	1.48	0.93
50	0.90	0.82	0.66	1.48	0.90
100	1.0	1.01	0.75	1.76	1.01

Fig. 3. SEM-EDX images of SmFeO_3 and 30 wt % $\text{Sm}_2\text{O}_3/\text{SmFeO}_3$ powders: (a) SEM image of the SmFeO_3 powder, (b) Fe mapping and (c) Sm mapping; and (d) SEM images of 30 wt % $\text{Sm}_2\text{O}_3/\text{SmFeO}_3$ powders, (e) Fe mapping and (f) Sm mapping.

Fig. 4. $\text{O}1\text{s}$ XPS spectra of the $\text{Sm}_2\text{O}_3/\text{SmFeO}_3$ (0–50 wt %) and Sm_2O_3 powders.

and its peak intensity became larger. This peak shift and intensity enlargement is unambiguously due to that the surface chemistry of the samples is influenced by Sm_2O_3 . So far, negatively charged adsorbed oxygen species on some oxides such as O^- and O_2^- have been reported.^{13),14)} These adsorbed oxygen species are fundamentally important for the semiconductors to be used for a chemo-resistive sensor, and have been investigated especially on SnO_2 based on the space charge layer theory.¹⁵⁾ Since O_2^- possesses a strong oxidation power, that species seems unlikely to be on the surface of Sm_2O_3 which solely has a poor oxidation activity for the VOCs. From the XPS result, binding energy for the lattice oxygen (O^{2-}) is almost identical in SmFeO_3 and Sm_2O_3 ; whereas, binding energy for the adsorbed oxygen on Sm_2O_3 is larger compared to SmFeO_3 . Summation of O_{ad} and $\text{O}_{\text{lattice}}$ was close to the stoichiometric amount (1.5) in all the samples. The concentrations of the adsorbed oxygen normalized with the concentration of Sm ($\text{O}_{\text{add}}/\text{Sm}$) are also shown in Table 1. The $\text{O}_{\text{add}}/\text{Sm}$ value increased with increasing Sm content. This suggests that the added Sm_2O_3 produces new oxygen adsorption sites.

3.2 Sensor responses

Figure 5 shows the transient sensor responses to 30 ppm toluene and ethanol. According to the p-type semiconducting feature, conductance was decreased by the toluene gas exposure. The Sm_2O_3 adding remarkably reduced the base conductance in air. This is probably due to that the added Sm_2O_3 particles having much lower conductivity are located at the grain boundary of the SmFeO_3 particles, resulting in partly severing the conduction paths. It was characteristic on the sensor response behavior that the SmFeO_3 adding notably shortened the recovery time upon the switching from the VOC contaminated air to the standard air. For both the VOCs, the 90%-recovery time was notably reduced with the increase in Sm contents. This result indicates that the adsorbed VOC and/or its partially oxidized molecules are easily replaced by oxygen on the Sm_2O_3 -added surface. Probably, the binding energy of the adsorbed VOC on the SmFeO_3 surface is relatively large so that the adsorbed VOC are not easily released into the gas phase. However, on the Sm_2O_3 -added surface, the adsorbed VOCs can migrate onto the Sm_2O_3 particles, which can be an additional recovery process. Since the conductivity of Sm_2O_3 is much lower than SmFeO_3 , the addition of Sm_2O_3 decreased the base conductance. The excess amount of Sm_2O_3 like 50 wt % induced the abrupt decrease in the conductance.

Figure 6 shows the sensor responses to 30 ppm toluene and ethanol. The Sm_2O_3 -adding also modified the sensor response to 30 ppm toluene. The response increased up to 30 wt %, and reversely decreased by further adding. On the other hand, the sensor response to ethanol slightly increased by 10 wt % adding, but it became nearly constant up to 30 wt %. By further addition of Sm_2O_3 , the response steeply decreased.

3.3 Catalytic activity

Catalytic activity for toluene oxidation was evaluated with the temperature for 50% VOC conversion, T_{50} . T_{50} values for the samples are shown in Fig. 7. T_{50} value significantly decreased with increasing Sm_2O_3 content up to 30 wt %, and increased again by further increase in the content. Although the catalytic activity of Sm_2O_3 is very poor, the adding Sm_2O_3 onto SmFeO_3 enhanced the catalytic activity. This result suggests that Sm_2O_3 itself has poor catalytic activity but it acts as a sort of promoter. It might be possible that the surface Sm–O may interact with toluene molecule to activate the C–H bond in toluene. Since the enrichment of

Fig. 5. Transient response curves of the sensors with the $\text{Sm}_2\text{O}_3/\text{SmFeO}_3$ semiconducting films on the sequential exposure to the air balanced 30 ppm VOCs and air: (a) 30 ppm toluene, and (b) 30 ppm ethanol.

Sm simultaneously enlarges the surface adsorbed oxygen as indicated in the XPS result, increasing Sm content should enhance the catalytic activity. Specific surface areas (SSA) of the powders are listed in **Table 2**. The SSA value of the SmFeO_3 powder is relatively small compared to the Sm_2O_3 added powders. We previously examined SSA of SmFeO_3 prepared from the cyano-complex at different calcination temperatures.¹⁶⁾ SSA value of SmFeO_3 was fairly dependent on the calcination temperature. In particular, SSA value steeply dropped at 800°C , owing to the grain-growth of SmFeO_3 . In the present study, Sm_2O_3 added powders have slightly larger SSA values compared to that of SmFeO_3 . This may suggest that the added Sm_2O_3 acts as a grain-growth inhibitor to some degree. The amounts of toluene adsorption on SmFeO_3 , 30 and 50 wt% Sm_2O_3 loaded SmFeO_3 were measured with the BET analysis (**Fig. 8**). The amount of toluene adsorption increased with an increase in the surface Sm content. This undoubtedly indicates that the surface Sm act as a toluene adsorption site. The amounts of toluene adsorption were 0.380

Fig. 6. Dependences of the amount of the Sm_2O_3 adding on the sensor responses to 30 ppm toluene and ethanol: (a) 30 ppm toluene, and (b) 30 ppm ethanol.

$\text{cm}^3(\text{STP})\text{g}^{-1}$ for SmFeO_3 , $0.622 \text{ cm}^3(\text{STP})\text{g}^{-1}$ for the 30 wt% and $1.047 \text{ cm}^3(\text{STP})\text{g}^{-1}$ for the 50 wt% Sm_2O_3 loaded samples. The small value of the toluene adsorption on the pure SmFeO_3 may be somewhat due to its small SSA value. However, the amount of toluene adsorption normalized with the concentration of Sm are $0.84 (\text{SmFeO}_3)$, $0.95 (30 \text{ wt}\%)$, and $1.33 \text{ cm}^3(\text{STP})\text{g}^{-1} (50 \text{ wt}\%)$, which increases with the Sm_2O_3 content. This result indicates that the Sm in Sm_2O_3 particles has larger affinity to toluene compared to that in SmFeO_3 . On the other hand, the amount of ethanol adsorption on SmFeO_3 was much larger than that of toluene: $0.380 \text{ cm}^3(\text{STP})\text{g}^{-1}$ for toluene and $0.855 \text{ cm}^3(\text{STP})\text{g}^{-1}$ for ethanol at 25°C . This can be the reason why the sensor responded better in ethanol than in toluene.

Previously, we examined CO oxidation activity of SmFeO_3 , and concluded that Fe could be an activation site for the oxidation reaction.¹⁶⁾ If this conclusion is also applicable for the current system, toluene molecules predominantly adsorb on the added Sm–O and diffuse onto the Fe activation sites. Excessive amount of Sm_2O_3 , that is more than 30 wt%, may block the Fe activation sites.

Fig. 7. Catalytic activity of the Sm₂O₃-added SmFeO₃ for the VOC oxidation: (a) 30 ppm toluene, and (b) 30 ppm ethanol.

Table 2. Specific surface area of the Sm₂O₃-loaded SmFeO₃ powders

Sm ₂ O ₃ contents (wt %)	Specific surface area (m ² /g)
0	3.6
10	6.4
20	8.5
30	7.9
40	7.6
50	7.2
100	7.4

4. Discussion

4.1 Effect of the Sm₂O₃ adding on the sensor properties

From the investigations in this study, it was found that the Sm₂O₃-adding increased the amount of adsorbed oxygen and VOC species as well as the surface Sm concentration. As a result, these increments remarkably modified the sensor response,

Fig. 8. The amounts of toluene adsorption on the Sm₂O₃-added SmFeO₃ evaluated with the BET analysis at 25°C.

recovery time and catalytic activity for the VOCs oxidation. Sm₂O₃ is well known as a catalyst for oxidative coupling of methane, which yields C₂H₆ and C₂H₄.¹⁷⁾ In the current case, Sm₂O₃ is hardly active around the sensing temperature for the oxidation of toluene and ethanol. Rather, it was suggested that Sm₂O₃ acts as a VOC adsorption site to condense the VOC molecules on the sensing layer. The effects on the sensor response and the catalytic activity were more pronounced in the case of toluene compared to ethanol on the surface of the SmFeO₃ sensor. The amount of ethanol adsorbed on the surface of SmFeO₃ is more than twice as that of toluene. Since affinity to ethanol on the surface of SmFeO₃ is essentially large, the increase in the Sm concentration is not so effective to increase the amount of ethanol adsorption. On the contrary, the Sm₂O₃-adding may partially block the active site (probably Fe) for ethanol oxidation. In fact, the Sm₂O₃-adding inhibited the ethanol oxidation activity.

The effect of Sm₂O₃-adding on the SnO₂ nanoparticle on the sensor response to VOCs was also reported.¹⁸⁾ In this report, the Sm₂O₃ adding effect was attributed to that increasing the number of oxygen vacancies and decreasing SnO₂ nanoparticles by the adding changed the reaction mechanism and catalytic activity; the BET surface area of the SnO₂ nanoparticles is 146 m²/g. In this study, the Sm₂O₃ particles are present on grain boundary of the SmFeO₃ particles, because the base resistance of the sensor increased with the Sm₂O₃ adding. However, the surface areas of the SmFeO₃ powder is very small (3.6 cm²/g), which means the particle size is relatively large, so that the SmFeO₃ particles are initially poor of sinterability compared to the reported case. Instead, the Sm₂O₃ adding, in this study, was more effective on the amount of VOC adsorption. Further investigation will be required to clarify VOC adsorption mechanism onto Sm of SmFeO₃ and Sm₂O₃. Since the Sm–O_{ad} bonding energy of Sm₂O₃ is larger than that of SmFeO₃, VOC molecule may not adsorb by replacing O_{ad}. Rather we speculate that VOC molecules occupy monodentately on O_{ad} or bidentately on Sm–O_{ad}.

5. Conclusion

Sm₂O₃ adding onto SmFeO₃ significantly enhanced the responses to 30 ppm toluene. The 30 wt % adding gave the maximum response but the further adding decreased the sensor

response. Catalytic activity for toluene oxidation showed the similar tendency to the sensor examination; it became the maximum at 30 wt % adding. The Sm₂O₃ adding enlarged the surface adsorbed oxygen and the amount of toluene adsorption. It was suggested that the surface Sm (or Sm–O_{ad}) should be a toluene adsorption site, and thus the Sm₂O₃ added surface was effective for catalytic activity and sensing of toluene. Since SmFeO₃ essentially possesses a large affinity to ethanol, the Sm₂O₃-adding was not effective for the ethanol sensing.

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