Nitromethane Sensing Characteristics of SnO$_2$ Gas Sensors and Infrared Spectroscopic Study

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Abstract: The SnO$_2$-based thick film sensors were fabricated by screen printing and dipping methods, and their sensing characteristics to CH$_3$NO$_2$ gas were investigated. The oxidation products of CH$_3$NO$_2$ on the thick film were analyzed by FT-IR using a heatable gas cell. The IR results showed that the products formed by oxidation of CH$_3$NO$_2$ at 300°C on the SnO$_2$/Al$_2$O$_3$/Pd thick film were mainly CO$_2$ and NH$_3$, while on the SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ thick film products such as CO$_2$, H$_2$O, N$_2$O, and NH$_3$ were observed. The thick film devices containing SiO$_2$ showed high selectivity and negative sensitivity to CH$_3$NO$_2$ due to the presence of nitrogen compounds produced by oxidation of CH$_3$NO$_2$. Optimum amount of Nb$_2$O$_5$ and operating temperature were 1.0 wt% and 300°C, respectively.

Keywords: oxidation of nitromethane, SnO$_2$-based sensor, FT-IR spectra, dipping of Si(C$_2$H$_5$O)$_3$.

Introduction

Gas sensors detecting a trace amount of the gases have applied to the process in industries of chemistry, pharmaceutical and fermentation in order to control the amount of the harmful wastes discharged from the plants, the explosion of the combustible gases and incomplete combustion, exhaust gases from automobiles, and testing in the clinics. The sensors show many advantages over optical or electrochemical sensors. The main advantages are their low cost, low consumption of electrical power, and high sensitivity.

The phenomenon of electrical conductivity changes induced in semiconducting materials by adsorption of gases on the solid surface is increasingly being used as a means of flammable and toxic gas detection. The working mechanism of thick-film and sintered gas sensors is based on the build up of Schottky barriers between adjacent grains caused by the ionosorbed oxygen [1].

Semiconductor gas sensors using SnO$_2$ and ZnO have been studied extensively since they were proposed by Seiyama and coworkers [2]. Successively, several research laboratories worked with the aim of developing new devices. The recent research on flammable gas sensors has concentrated on SnO$_2$ in the form of thick-film and sintered ceramics [3-9]. Also, a large amount of research has been devoted to SnO$_2$ thin films these last years [10-13].

However, sensors should be improved due to a lack of stability and a poor selectivity. The addition of small amounts of additives is known to provide better sensitivity and selectivity [14,15]. An improvement of the selectivity of sensors based on SnO$_2$ is generally obtained by adding some specific catalysts such as Pd or Pt for heavy combustible gases [8,16,17], CeO$_2$ for hydrogen [18], and Nb$_2$O$_5$ for CO and NH$_3$ [19].

In this work, we have developed a SnO$_2$-based sensor for the detection of nitromethane gas which is known to be a poisonous chemical at low level in air. Nitromethane is known to be an intermediate in the SCR of NOx with methane, which derivatives cause deactivation by blocking zeolite channels [20,22]. The sensing characteristics of a SnO$_2$-based sensor to nitromethane were studied by FT-IR analyses of gaseous species produced by oxidation of nitromethane on the sensor surface.

Experimental

Al$_2$O$_3$ (10.0 wt%) and Nb$_2$O$_5$ (0.2–2.0 wt%) were
mechanically mixed with the base material, SnO₂, followed by calcination in air at 600°C for 1 hr. Al₂O₃, Nb₂O₅, and SnO₂ were obtained from Aldrich Co. USA, where the purity of the samples was 99.9%. α-Al₂O₃ was used to improve the stability of fabricated sensor and to give a strong cohesion between thick film and alumina substrate. Nb₂O₅ was used to enhance the selectivity of gas sensor to acetonitrile. The calcined sample was ground and then mixed with water to prepare paste. The paste was screen-printed onto an alumina substrate and then dipped into tetraethylorthosilicate solution followed by sintering in air at 700°C for 1 hr. Figure 1 shows the fabrication process of the thick film sensor.

The structure of sensing device is shown in Figure 2, where gold electrode was connected with platinum wire. The size of gas sensor was 4 x 4 x 0.5 mm³ and the electric power was about 0.85 Watt to keep the temperature of gas sensor constant as 300°C. Liquid nitromethane was injected into a stainless box (30 x 30 x 30 cm³) containing 1 atm of air through injection rubber tube to obtain the desired concentration of nitromethane for the measurement of sensitivity. The sensor sensitivity was measured in a box equipped with a heater. The sensitivity is defined as R/Rₓ where Rₓ and R are the electric resistances in the test gas and in fresh air, respectively.

The products formed by the oxidation reaction of CH₃NO₂ on the sensor surface were analyzed by a Mattson Model GL 6030E FT-IR spectrometer using a heatable IR gas cell with the volume of 270 mL. FT-IR absorption spectra were measured over the range of 4000 ~ 400 cm⁻¹ at room temperature after the reaction at high temperature for 0.5 hr. The specific surface area was determined by applying the BET method to the adsorption of N₂ at -196°C [23-25]. SnO₂-based samples were checked in order to determine their structures by means of a Jeol Model JDX-8030 diffractometer, employing CuKα (Ni-filtered) radiation (1.5405 Å).

**Results and Discussion**

Specific surface areas of some samples are listed in Table 1. The surface area of SnO₂ was 5.0 m²/g, while those of SnO₂/Al₂O₃/Pd and SnO₂/Al₂O₃/Nb₂O₅ were 10.5 and 22.0 m²/g, respectively. The surface area of SnO₂/Al₂O₃/Nb₂O₅/SiO₂ is remarkably large compared to the other samples. It seems likely that the high surface area of SnO₂/Al₂O₃/Nb₂O₅/SiO₂ is responsible for the addition of SiO₂ and that the surface area also influences
Table 1. Specific Surface Areas of Some Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>5.0</td>
</tr>
<tr>
<td>SnO₂/Al₂O₃/Pd</td>
<td>10.5</td>
</tr>
<tr>
<td>SnO₂/Al₂O₃/Nb₂O₅</td>
<td>22.0</td>
</tr>
<tr>
<td>SnO₂/Al₂O₃/Nb₂O₅/SiO₂</td>
<td>84.6</td>
</tr>
</tbody>
</table>

the sensing characteristics of sensor, as described later.

The crystalline structures of SnO₂/Al₂O₃/Nb₂O₅ and SnO₂/Al₂O₃/Nb₂O₅/SiO₂ sintered in air at 700°C for 1 hr were examined by X-ray diffraction method. As shown in Figure 3, there were only two phases of tetragonal SnO₂ and α-Al₂O₃. The crystalline phases of Nb₂O₅ and SiO₂ did not appear, indicating that they are amorphous or the crystallites formed are less than 4 nm in size, that is, beyond the detection capability of the XRD technique [26].

Figure 4 shows the IR spectra of CH₃NO₂ (20 torr) and the oxidation products of CH₃NO₂ on a SnO₂/Al₂O₃/Pd thick film under the condition of CH₃NO₂ 20 torr and air 20 torr at 300°C for different times. For pure CH₃NO₂, the band at 1594 cm⁻¹ is assigned to NO₂ asymmetric stretching vibration mode, while that at 1389 cm⁻¹ is ascribed to the NO₂ symmetric stretching mode [27,28]. The band at 2963 cm⁻¹ is assigned to CH₃ stretching vibration mode. However, on the SnO₂/Al₂O₃/Pd thick film, the bands due to NH₃ and CO₂ in addition to CH₃NO₂ were observed as shown in Figure 4. The bands at 3414, 1624, 964, and 930 cm⁻¹ are ascribed to the NH₃, while those at 3723, 3635, 2361, and 667 cm⁻¹ are due to the CO₂ [27,28]. As shown in Figure 4, the band intensities increased with reaction time, showing that large amount of CO₂ and NH₃ was produced after reaction for 1 hr. Oxidation of CH₃NO₂ on the SnO₂/ Al₂O₃/Pd seems to proceed by the following reaction.

\[ \text{CH}_3\text{NO}_2 = \text{NH}_3 + \text{CO}_2 \]  \[ (1) \]

It is well known that Pd and Pt are very active catalyst for a variety of oxidation reactions [29-31]. The
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Figure 5. Pd 3d XPS of SnO₂/Al₂O₃/Pd (0.2 wt%) sintered at 700°C.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Centre (eV)</th>
<th>FWHM (eV)</th>
<th>Height (%)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd⁴⁺</td>
<td>333.7</td>
<td>1.56</td>
<td>55</td>
<td>29</td>
</tr>
<tr>
<td>Pd²⁺</td>
<td>336.2</td>
<td>1.92</td>
<td>87</td>
<td>56</td>
</tr>
<tr>
<td>Pd⁰</td>
<td>334.8</td>
<td>1.70</td>
<td>26</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 6. Sensitivity of the SnO₂/Al₂O₃/Pd (0.2 wt%) thick film device to CH₃NO₂ at different operating temperatures.

Figure 6.

Figure 7 shows IR spectra of oxidation products of CH₃NO₂ on SnO₂/Al₂O₃/Nb₂O₅ at 300°C for different times. On SnO₂/Al₂O₃/Nb₂O₅, the bands (3723, 3635, 2361, 667 cm⁻¹) due to CO₂ and the bands (3414, 3334, 964, 930 cm⁻¹) due to NH₃ were observed similarly to the case of SnO₂/Al₂O₃/Pd in Figure 4. However, on SnO₂/Al₂O₃/Nb₂O₅ thick film, N₂O bands in addition to CO₂ and NH₃ bands appeared at 2238 and 2211 cm⁻¹ [27,28]. N₂O seems to be formed by the oxidation of NH₃ produced by equation (1) as the follows.

\[ 2\text{NH}_3 + \text{O}_2 = \text{N}_2\text{O}_2 + 3\text{H}_2\text{O} \] (2)

Oxidation of CH₃NO₂ on SnO₂/Al₂O₃/Nb₂O₅/SiO₂ thick film also produced CO₂, NH₃, H₂O, and N₂O similarly to the case of SnO₂/Al₂O₃/Nb₂O₅, as shown in Figure 8. However, the oxidation reaction of CH₃NO₂ on SnO₂/Al₂O₃/Nb₂O₅/SiO₂ proceeded easily compared to SnO₂/Al₂O₃/Nb₂O₅, which is probably due to the effect of additive, SiO₂.

NH₃ oxidation was carried out in a gas cell to examine the behavior of NH₃ produced on the thick film, where the concentrations of NH₃ and air were 20 torr and 300 torr, respectively. The results are illustrated in Figure 9. After reaction of NH₃ on SnO₂/Al₂O₃/Nb₂O₅ at 300°C for
1 hr, other products except NH$_3$ were not detected, while at 350°C the bands of H$_2$O (3450 and 1587 cm$^{-1}$) and N$_2$O (2238, 2211 cm$^{-1}$ doublet and 1300, 1273 cm$^{-1}$ doublet) appeared. These results indicate that NH$_3$ is oxidized by the above equation (2) and the reaction occurs to a greater extent at 350°C than at 300°C. On the other hand, oxidation of NH$_3$ on SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ proceeded very easily even at 300°C, as shown in Figure 9(c). Considering that the operating temperature of sensor is 300°C, it is expected that addition of SiO$_2$ gives a significant effect on the characteristics and sensing selectivity of a SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$ sensor.

We examined the dependence of Nb$_2$O$_5$ level (0.2–2.0 wt%) on the sensitivity of SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ sensor under the condition of 1 atm air, when the concentration of CH$_3$NO$_2$ was 30 ppm and the operating temperature was 300°C. As shown in Figure 10, the devices gave the highest sensitivity at 1.0 wt% Nb$_2$O$_5$, showing the lowest sensitivity at 0.2 wt%.

The sensitivity of the SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ device are illustrated as a function of CH$_3$NO$_2$ concentration at different operating temperatures in Figure 11. The sensitivity increased with increasing the concentration of CH$_3$NO$_2$ and the optimum operating temperature was 300°C. It seems likely that the formation of large amounts of nitrogen compounds such as N$_2$O and NH$_3$ which decrease the electric conductivity [35], as shown in Figure 7, is responsible for the decreased sensitivity at 350°C. Figure 12 shows sensing characteristics of the SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ device to various gases at the operating temperature of 300°C. The device exhibited the positive characteristic, resistance decrease, upon exposure to CO, NO$_2$, C$_6$H$_5$NO$_2$ and C$_6$H$_5$OH, while the device exhibited negative characteristic upon exposure to CH$_3$NO$_2$ and SO$_2$. These results are in good agreement with the fact that, as shown in Figure 8, SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ produce N$_2$O and NH$_3$ which decrease the electric conductivity of sensor [35]. Therefore, gas sensor
Figure 9. Infrared spectra after oxidation reaction of NH$_3$ on (a, b) SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$ and (c) SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$.

Figure 10. Sensitivity of the SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ thick film device containing different Nb$_2$O$_5$ contents to CH$_3$NO$_2$ at 300°C.

Figure 11. Sensitivity of the SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ thick film device as a function of CH$_3$NO$_2$ concentration at different operating temperatures.

Figure 12. Sensitivity of the SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ thick film device to various gases at 300°C.
shows high sensitivity and selectivity to CH$_3$NO$_2$.
In the transient response characteristics, the SnO$_2$/
Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ sensor was very sensitive to low gas
concentration (3~20 ppm). Also, the sensor showed
excellent recovery characteristics as the operating
temperature increased. At 300°C, the response and
recovery times are 3 sec and 10 min, respectively.

Conclusion

The SnO$_2$-based thick film devices for the detection of
CH$_3$NO$_2$ were fabricated by the screen printing and
dipping methods. The oxidation products of CH$_3$NO$_2$ on
SnO$_2$/Al$_2$O$_3$/Nb$_2$O$_5$/SiO$_2$ thick film were CO$_2$, H$_2$O, and
NH$_3$. The oxidizing agents such as NO$_2$ and NH$_3$ formed
by oxidation of CH$_3$NO$_2$ played an important role in
determining sensitivity and selectivity to CH$_3$NO$_2$. The
response time and the optimum operating temperature
were 3 sec and 300°C, respectively.

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