Effects of Calcination Temperature and Acid-Base Properties on Mixed Potential Ammonia Sensors Modified by Metal Oxides

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Abstract: Mixed potential sensors were fabricated using yttria-stabilized zirconia (YSZ) as a solid electrolyte and a mixture of Au and various metal oxides as a sensing electrode. The effects of calcination temperature ranging from 600 to 1,000 °C and acid-base properties of the metal oxides on the sensing properties were examined. The selective sensing of ammonia was achieved by modification of the sensing electrode using MoO₃, Bi₂O₃ and V₂O₅, while the use of WO₃, Nb₂O₅ and MgO was not effective. The melting points of the former group were below 820 °C, while those of the latter group were higher than 1,000 °C. Among the former group, the selective sensing of ammonia was strongly dependent on the calcination temperature, which was optimum around melting point of the corresponding metal oxides. The good spreading of the metal oxides on the electrode is suggested to be one of the important factors. In the former group, the relative response of ammonia to propene was in the order of MoO₃ > Bi₂O₃ > V₂O₅, which agreed well with the acidity of the metal oxides. The importance of the acidic properties of metal oxides for ammonia sensing was clarified.

Keywords: ammonia sensor; metal oxide; YSZ; acidity; melting point
1. Introduction

The Urea-SCR (Selective Catalytic Reduction) technique is known to be an effective technology for the removal of nitrogen oxide (NOx) emissions from heavy-duty diesel engine cars [1-4]. In this system, an aqueous solution of urea is injected into a catalytic converter, hydroxylation of urea in the converter results in the formation of NH₃, and the thus formed NH₃ then successfully reduces NOx to N₂ over Fe-zeolite or vanadium-based catalysts in a wide range of temperatures. The urea-SCR system has been already put into practical application, however, monitoring of the NH₃ concentration in the catalytic converter is required to achieve proper operation of a urea-SCR system. For the practical application of the ammonia sensors to automobile exhausts, sufficient response altitude and cross-sensitivity, quick response, and tolerance to high temperatures under hydrothermal conditions are required.

Various types of ammonia sensors have been proposed [5,6]. The ammonia sensors using surface proton-conducting metal oxides, such as zeolites [7,8] and WOₓ/ZrO₂ [9,10], show excellent cross-sensitivity to NH₃ in the presence of various interfering gases, such as hydrocarbons, CO, and NOx. However, these materials have high surface area, and consequently they should have low thermal stability. Semiconductors of n-type metal oxides such as WO₃ [11], MoO₃ [12-15], V₂O₅ [16,17], SnO₂ [18,19], TiO₂ [20], In₂O₃ [21-23] and Ru/ZnO [24] have high hydrothermal stability, and have been extensively investigated as sensing materials. They usually act at lower temperatures (below 300 °C) than those needed in the automobile industry, but show low cross-sensitivity to NH₃ in the presence of various interfering gases. Consequently, it is highly desirable to develop thermally stable ammonia sensors which show high cross-sensitivity to NH₃ at high temperatures.

Mixed potential sensors are thought to be one of the promising technologies for this purpose because they are used at high temperatures around 500–600 °C. They are usually applied to sensors for CO and hydrocarbons [25-38], however, selective ammonia sensors can be designed by selection of appropriate sensing materials. Wang et al. examined various metals and metal oxides as sensing electrodes for ammonia sensors, and demonstrated that V₂O₅, BiVO₄, MoO₃, and WO₃ are all effective for the sensing of NH₃ [39]. Especially, BiVO₄ showed the best output voltage in the presence of NH₃, which was far higher than those of CO, C₃H₆, and NO. Schö nauer and co-workers developed a novel selective ammonia sensor based on the mixed potential effect using a porous V₂O₅-WO₃-TiO₂-based SCR catalyst as a sensing material [40]. The proposed sensor showed good cross-sensitivity to NH₃, and they demonstrated that the sensor can detect very small NH₃ slips at the downstream of a real SCR catalyst. Elumalai et al. fabricated a planar mixed-potential-type sensor using a YSZ electrolyte and NiO/Au sensing electrode [41]. The sensor exhibited good sensitivity and cross-sensitivity to NH₃ at 800 °C under wet conditions, i.e., the emf response to 100 ppm NH₃ was about −34 mV, while the cross-sensitivities to the other examined gases were about ±5 mV or negligible. Hibino et al. prepared a proton-conducting thin Zr₁−xYₓP₂O₇ film on a YSZ substrate by reacting with liquid H₃PO₄ [42]. This sensor yielded a remarkably sensitive and selective response to low concentrations of NH₃. Their approach suggests a strong contribution of acidity to selective NH₃ detection.

It can be expected that the acid properties of the sensing material is one of the important factors for better cross-sensitivity because NH₃ is a basic molecule, while the other interfering gases, CO, HC, and NOx, are not. However, the effects of the acid-base properties of sensing materials have not been
clarified. The aim of this study was to obtain knowledge for the design of a metal oxide-modified mixed potential ammonia sensor. From the relationships between sensing properties and character of the metal oxides, the important factors for the selective sensing of NH$_3$ are clarified.

2. Experimental Section

2.1. Materials Synthesis and Sensor Setup

MnO$_2$, MoO$_3$, Bi$_2$O$_3$, WO$_3$, Nb$_2$O$_5$, and MgO (99% purity) were purchased from Kishida Chemical Co., Ltd. V$_2$O$_5$ (99% purity) was purchased from Mituswa Chemical Co., Ltd. BiVO$_4$ was prepared by milling V$_2$O$_5$ and Bi$_2$O$_3$ for 24 h, followed by calcination of the mixture at 900 °C.

The schematic structure of the two-chamber cell constructed with a YSZ solid electrolyte on an alumina substrate is illustrated in Figure 1. One side of the YSZ solid electrolyte covered by a Pt electrode is exposed to the inside chamber with outside air. Another side of the YSZ solid electrolyte is covered with a mixture of Au and metal oxide thick film as a sensing material prepared by the screen-printing technique in the same manner reported previously [9,10,17]. For the preparation of electrodes, screen printable pastes were produced by mixing gold paste (purchased from Daiken Chemical Co., Ltd., Au100-1) with 10 wt% of the metal oxide powders. The sensor was calcined in air for 5 h at 650–1,000 °C depending on the metal oxide use, and assembled in a stainless case. Thickness of the film after the calcination step was ca. 10–20 μm. The name of each sensor electrode is abbreviated as the name of the metal oxide and calcination temperature in °C, for example, Bi$_2$O$_3$(850).

**Figure 1.** Schematic representation of the sensor examined in the present study.
2.2. Gas Sensor Measurements

Sensing characteristics were evaluated by using a conventional gas-flow apparatus equipped with a furnace operating at 600 °C. The stainless flow cell was heated at operating temperatures. The reference electrode (cathode) was exposed to air, and the sensing electrode (anode) was exposed to a flow of mixture gas. The composition of the base gas is 10% O₂, 3% H₂O, and N₂ as a balance gas at a flow rate of 150 cm³ min⁻¹. The standard concentrations of NH₃ and C₃H₆ are 500 ppm. The electromotive forces (EMF) value of the cell was measured by an electrometer (Hokuto Denko HZ-5000).

3. Results and Discussion

3.1. Effect of Calcination

Figure 2 shows an example of transient response of Bi₂O₃(850) to the injection of ammonia and C₃H₆. Due to the difference in the oxygen concentration (20% at the reference electrode and 10% at the sensing electrode), the EMF of the sensor electrode is −15.5 mV in the absence of reducing gases. In the presence of 500 ppm C₃H₆, EMF decreased to −19.1 mV. The difference in EMF between those in the presence and absence of a probe molecule is determined as ΔEMF, 3.6 mV in this case, and used as an indicator of response height. On the other hand, the ΔEMF in a flow of the same amount of NH₃ was −68.2 mV, which is one order higher than that in C₃H₆, indicating the very high selective sensing of the Bi₂O₃(850) electrode. After the evacuation of NH₃, the EMF value quickly recovered to the original level. The ΔEMF of NH₃ relative to that of the same concentration of C₃H₆ (ΔEMF₁ ⁄ ΔEMF₂) is used as a measure of cross-sensitivity.

![Figure 2](image)

The cross-sensitivity strongly depended on the calcination temperatures of the electrodes. In Figure 3, the ΔEMF₁ ⁄ ΔEMF₂ ratios of the selected sensors as a function of the calcination temperature are shown. V₂O₅, MoO₃, and Bi₂O₃ showed the maximum ΔEMF₁ ⁄ ΔEMF₂ at 700, 800, and 850 °C, respectively. Since the melting points of these metal oxides are 695, 790, and 820 °C, the maximum cross-sensitivity was observed around their melting points.
Figure 3. The relative ΔEMF as a function of calcination temperature of sensing electrodes.

Table 1. Summary of ΔEMF to 500 ppm of NH₃ and C₃H₆ at 600 °C on the sensor electrode covered with mixtures of Au and various metal oxides.

| Electrode    | m.p. of MOx | Calcination/°C | ΔEMF₂NH₃ | ΔEMF₂C₃H₆ | ΔEMF₂NH₃/ΔEMF₂C₃H₆ |
|--------------|-------------|----------------|----------|-----------|-------------------|
| MnO₂(700)    | 535         | 700            | 176      | 19.6      | 9.0               |
| V₂O₅(700)    | 690         | 700            | 188      | 33.2      | 5.7               |
| MoO₃(800)    | 795         | 800            | 336      | 9.5       | 35.5              |
| Bi₂O₃(850)   | 820         | 850            | 68.2     | 3.6       | 18.9              |
| WO₃(1000)    | 1,470       | 1,000          | 50.9     | 30.5      | 1.7               |
| Nb₂O₅(1000)  | 1,520       | 1,000          | 224      | 190       | 1.3               |
| MgO(1000)    | 2,800       | 1,000          | 190      | 146       | 1.3               |
| Au only      | (1,064)     | 1,000          | 89.4     | 71.3      | 1.3               |

Various kinds of the sensing electrodes listed in Table 1 were prepared using the corresponding metal oxides. Due to the strong dependence of the cross-sensitivity on calcination temperatures as shown in Figure 3, the sensing performances were compared after the calcination at the optimum temperatures ranging from 700 to 1,000 °C. For WO₃(1000), Nb₂O₅(1000), and MgO(1000) electrodes, the ΔEMF₂NH₃/ΔEMF₂C₃H₆ ratios were comparable to that of the electrode without modification (Au only). This implies a negligible chemical interaction between Au and metal oxides, which results in the ΔEMF₂NH₃/ΔEMF₂C₃H₆ ratio of around unity and thus, non-selective NH₃ detection. Melting points of these metal oxides were higher than the calcination temperature of 1,000 °C.

On the other hand, very high ΔEMF₂NH₃ and low ΔEMF₂C₃H₆ were obtained when MoO₃ was used as a sensing material. As a result, the ΔEMF₂NH₃/ΔEMF₂C₃H₆ ratio was the highest for MoO₃(800). MnO₂, V₂O₅, and Bi₂O₃ also showed high ΔEMF₂NH₃/ΔEMF₂C₃H₆ ratios and sufficient ΔEMF values in the presence of NH₃. In these metal oxides melting points were below 820 °C, and the calcination temperatures were optimized around their melting points. The results show that the melting point of the sensing material is one of the important factors for the preparation of the selective sensors.

The maximum cross-sensitivity at around the melting points of the metal oxides suggests that the good mixing of the metal oxides, Au electrode, and YSZ is essential for selective NH₃ detection. It can be speculated that the acidic metal oxides are well spread on Au and YSZ surface and achieved the
successful modification of Au and YSZ. Above the melting points, too much spreading of the metal oxide results in the undesired covering of Au and YSZ electrode. The strong dependence of the selective sensing of NH$_3$ on the calcination temperature suggests that the spreading of metal oxide is important for the successful preparation of the sensor. As shown in Table 1, MoO$_3$(850) showed the highest response altitude and $\Delta$EMF$_{NH3}$/EMF$_{C3H6}$ ratio. However, owing to sublimation of MoO$_3$ at 1,155 °C [43], MoO$_3$ is not suitable for the application of ammonia sensing in automobile exhaust systems. Therefore, further investigations have been done by using Bi$_2$O$_3$(850) which showed the second highest $\Delta$EMF$_{NH3}$/EMF$_{C3H6}$ and sufficient response altitude.

### 3.2. Effect of Acid-Base Property

Figure 4 shows $\Delta$EMF$_{NH3}$/EMF$_{C3H6}$ ratio of MoO$_3$(800), Bi$_2$O$_3$(850) and V$_2$O$_5$(700) as a function of electronegativity of the metals in the metal oxides. As we have reported in a previous paper [17], the electronegativity can be used as an indicator of the acid-base properties of metal oxides: the higher electronegativity implies higher acidity of the oxides. Clearly, the $\Delta$EMF$_{NH3}$/EMF$_{C3H6}$ ratio increased with the electronegativity. This correlation shows that the acidity of metal oxide is very essential for the cross-sensitivity to NH$_3$.

**Figure 4.** The relative $\Delta$EMF as a function of electronegativity of added metal oxides.

The importance of acid-base properties also can be seen in the effect of the acid-base properties of probe molecules shown in Figure 5. The proton affinity is a good indicator for the acid-base properties of molecules [44]. The Bi$_2$O$_3$(850) electrode was not sensitive to H$_2$, NO, CO, C$_3$H$_6$ having lower proton affinity. However, $\Delta$EMF became very high to NH$_3$ and pyridine which have high proton affinity, *i.e.*, are highly basic molecules. These results clearly indicate that the sensing response of the prepared electrodes strongly depends on the acid-base interaction of the sensing electrodes and probe molecules. A highly acidic property is required for the selective detection of NH$_3$. 
Figure 5. The ΔEMF in the presence of 500 ppm of various gases as a function of the proton affinity.

3.3. Performance of Bi$_2$O$_3$(850) as an Ammonia Sensor

The sensing performance of Bi$_2$O$_3$(850) as an ammonia sensor was investigated. The response of the Bi$_2$O$_3$(850) electrode was examined by stepwise change in the NH$_3$ concentration up to 1,000 ppm. The measured ΔEMF was plotted as a function of NH$_3$ concentration in Figure 6. The sensor characteristic was semi-logarithmic to the NH$_3$ concentration. This means that the sensor has a high sensitivity, even at lower ammonia concentrations.

Figure 6. ΔEMF of Bi$_2$O$_3$(850) electrode as a function of NH$_3$ concentration at 600 °C.

The mixed potential mechanism was evaluated for the Bi$_2$O$_3$(850) electrode by modified polarization curves [25-27] in 10% O$_2$ and in 500 ppm NH$_3$ at 600 °C, in the same manner proposed by Miura [25]. The intersection of the polarization curves was observed at the same ΔEMF value in the presence of the same concentrations of NH$_3$ and O$_2$. When the following Equation (1) at the cathode and Equation (2) at the anode proceed at an equal rate, an electrode potential shows the mixed potential:

\[
\frac{1}{2} O_2 + 2 e^- \rightarrow O^{2-} \quad (1)
\]

\[
\frac{2}{3} NH_3 + O^{2-} \rightarrow \frac{1}{3} N_2 + H_2O + 2 e^- \quad (2)
\]
It is important to examine the effect of interfering gaseous species on the response of the sensor. Figure 7 shows the influence of the concentration of O$_2$ and water vapor on the responses of the Bi$_2$O$_3$(850) electrode to 500 ppm NH$_3$. It should be noted that a different lot of the Bi$_2$O$_3$(850) sensor was used in this section, and the sensing responses were compared with those of BiVO$_4$(750) electrode, which is known as one of the excellent electrode for NH$_3$ sensing [39], prepared by the same manner reported by Wang et al. [39]. The concentration of water vapor was varied from 1 to 10%. The responses of both the sensors were not much affected by water vapor. While, the higher concentration of O$_2$ slightly decreased the $\Delta$EMF vale of the Bi$_2$O$_3$(850) electrode, though the $\Delta$EMF of the BiVO$_4$(750) electrode significantly decreased when the O$_2$ concentration is 15%. The Bi$_2$O$_3$(850) electrode is less interfered by the concentration of O$_2$ than the BiVO$_4$(750) electrode.

![Figure 7](image_url) Influence of O$_2$ and water vapor on the response of the Bi$_2$O$_3$(850) and BiVO$_4$(750) electrodes to 500 ppm NH$_3$ at 600 °C.

4. Conclusions

The effect of calcination temperature and acid-base properties of metal oxides used as a sensing material for an ammonia sensor have been investigated. The sensor electrode was prepared by the two-chamber cell constructed from a YSZ solid electrolyte, on which one side is covered by a Pt electrode and another side is covered with a mixture of Au and a metal oxide thick film as a sensing material. When MoO$_3$, Bi$_2$O$_3$ and V$_2$O$_5$, having melting points below 820 °C, are used as the sensing material, the sensors exhibited very high cross-sensitivity to NH$_3$. The use of WO$_3$, Nb$_2$O$_5$ and MgO having melting points above 1,000 °C as sensing materials was not effective. The good spreading of the metal oxide on the sensing electrode was suggested to be one of the important factors. The sensing selectivity to ammonia was in the order of MoO$_3$ > Bi$_2$O$_3$ > V$_2$O$_5$, which was in agreement with the corresponding acidity of the metal oxides. It was clarified that the acidity of metal oxides is the determining factor for the selective sensing of NH$_3$. 

| O$_2$ concentration /% | BiVO$_4$ | Bi$_2$O$_3$ |
|------------------------|---------|-----------|
| 0                      | 300     | 200       |
| 5                      | 200     | 100       |
| 10                     | 100     |            |
| 15                     | 0       | 0         |
| 20                     | 0       | 0         |

| H$_2$O concentration /% | BiVO$_4$ | Bi$_2$O$_3$ |
|-------------------------|---------|-----------|
| 0                       | 300     | 200       |
| 2                       | 200     | 100       |
| 4                       | 100     |           |
| 6                       | 0       | 0         |
| 8                       | 0       | 0         |
| 10                      | 0       | 0         |
| 12                      | 0       | 0         |
| 14                      | 0       | 0         |
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